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A coordinatively flexible hexadentate ligand gives structurally isomeric complexes $M_2(L)X_3$ (M = Cu, Zn; X = Br, Cl)

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Polypyridyl multidentate ligands based on ethylenediamine backbones are important metal-binding agents with applications in biomimetics and homogeneous catalysis. The seemingly hexadentate tpena ligand [systematic name: *N*,*N*,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine-*N*′-acetate] reacts with zinc chloride and zinc bromide to form trichlorido[μ-*N*,*N*,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine-*N*′-acetato]dizinc(II), $[Zn_2(C_{22}H_{24}N_5O_2)Cl_3]$, and tribromido[$\mu$-*N*,*N*,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine-*N*′-acetato]dizinc(II), $[Zn_2Br_3(C_{22}H_{24}N_5O_2)]$. One Zn^{II} ion shows the anticipated N_5O coordination in an irregular six-coordinate site and is linked by an *anti* carboxylate bridge to a tetrahedral ZnX_3 (X = Cl or Br) unit. In contrast, the Cu^{II} ions in aquatribromido[μ-*N*,*N*,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine-*N*′-acetato]-dicopper(II)–tribromido[μ-*N*,*N*,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine-*N*′-acetato]dicopper(II)–water (1/1/6.5) $[Cu_2Br_3(C_{22}H_{24}N_5O_2)][Cu_2Br_3(C_{22}H_{24}N_5O_2)(H_2O)]\cdot 6.5H_2O$, occupy two tpena-chelated sites, one a trigonal bipyramidal N_3Cl_2 site and the other a square-planar N_2OCl site. In all three cases, electrospray ionization mass spectra were dominated by a misleading ion assignable to $[M(\text{tpena})]^+$ (M = Zn^{2+} and Cu^{2+}).

1. Introduction

Polypyridyl multidentate ligands based on ethylenediamine backbones are an important class of metal-binding agent with particular applications in biomimetics and homogeneous catalysis. We have introduced derivatives of this class of ligand which incorporate a single amino acid group and employed them to prepare model complexes for redox-active non-heme sites in metalloenzymes. Functional biomimetic and catalytic reactivity, for example, in the activation of O_2 and H_2O, has been demonstrated (Poulsen *et al.*, 2005; Nielsen *et al.*, 2006; Vad *et al.*, 2011, 2012; Lennartson & McKenzie, 2012; de Sousa *et al.*, 2015; Deville *et al.*, 2015). Dangling pyridines and the carboxylate groups are proposed to assist in proton transfer and the carboxylate group can be either terminal or bridge between metal ions to form oligomers and polymers (Berggren *et al.*, 2009; Egdal *et al.*, 2011). The latter has proven to be an advantage for achieving stability of Mn^{II} complexes towards air oxidation. If bridging does not occur, noncoordinated carboxylate O atoms are usually involved in hydrogen bonding in the solid state and these interactions may be important for solution-state reactivity, for example, in proton transfer (Vad *et al.*, 2012).

The structures of the redox-stable copper(II) and zinc(II) complexes of the ligand *N*,*N*,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine-*N*′-acetate (tpena) reported here are important for predicting the structures of more reactive redox-active systems

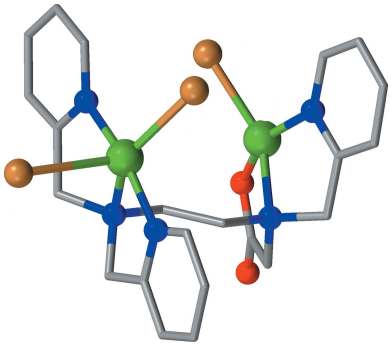


Table 1
Experimental details.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$[Zn_2(C_{22}H_{24}N_5O_2)Cl_3]$	$[Zn_2Br_3(C_{22}H_{24}N_5O_2)]$	$[Cu_2Br_3(C_{22}H_{24}N_5O_2)]$-$[Cu_2Br_3(C_{22}H_{24}N_5O_2)$-$(H_2O)]\cdot 6.5H_2O$
M_r	627.55	760.93	1649.66
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, $Pca2_1$	Triclinic, $P\overline{1}$
Temperature (K)	180	180	180
a, b, c (Å)	9.4985 (8), 11.3423 (10), 23.3697 (18)	18.7061 (12), 13.3342 (9), 20.4516 (13)	11.2516 (9), 15.0606 (10), 18.3213 (14)
α, β, γ (°)	90, 98.263 (4), 90	90, 90, 90	112.087 (3), 94.380 (3), 90.486 (3)
V (Å^3)	2491.6 (4)	5101.3 (6)	2866.1 (4)
Z	4	8	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.28	6.61	5.71
Crystal size (mm)	0.31 × 0.19 × 0.15	0.17 × 0.08 × 0.05	0.20 × 0.11 × 0.05
Data collection			
Diffractometer	Bruker–Nonius X8 APEXII CCD diffractometer	Bruker–Nonius X8 APEXII CCD diffractometer	Bruker–Nonius X8 APEXII CCD diffractometer
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*SADABS*; Krause *et al.*, 2015)	Multi-scan (*TWINABS*; Sheldrick, 2012)
T_{min}, T_{max}	0.469, 0.745	0.365, 0.431	0.303, 0.430
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	77315, 5051, 4340	127653, 11284, 8558	11068, 11068, 7261
R_{int}	0.084	0.081	0.077
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.629	0.669	0.625
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.099, 1.14	0.040, 0.078, 1.02	0.054, 0.114, 1.00
No. of reflections	5051	11284	11068
No. of parameters	307	614	686
No. of restraints	0	1	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.85, −0.48	1.26, −0.61	0.99, −0.88
Absolute structure	–	Refined as an inversion twin	–
Absolute structure parameter	–	0.245 (12)	–

Computer programs: *APEX2* (Bruker, 2012), *SAINT* (Bruker, 2012), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *SHELXTL* (Bruker, 2012), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

of earlier transition metal ions. They reveal two new structural prototypes, albeit with identical stoichiometry, thereby illustrating the coordinative flexibility of this ligand (see Scheme).

2. Experimental

2.1. Synthesis and crystallization

The copper and zinc halide complexes of tpena were prepared by mixing an aqueous solution (1 ml) of Na(tpena)-(CH_3CH_2OH) (0.048 mmol) (Vad *et al.*, 2011) with two equivalents of the appropriate dibromide or dichloride (0.097 mmol) dissolved in MeOH (2 ml). Upon slow evaporation of the solvent, either colourless crystals of the zinc or turquoise crystals of the copper complexes formed over a period of several days. These were isolated by filtration and washed with cold H_2O (yields 70–90%). IR (KBr disc): Zn_2(tpena)Cl_3, $\nu_{as(COO)}$ = 1602 cm^{-1}; Zn_2Br_3(tpena), $\nu_{as(COO)}$ = 1605 cm^{-1}; Cu_2Br_3(tpena)$(H_2O)_{3.75}$, $\nu_{as(COO)}$ = 1611 cm^{-1} (the spectra are available in the *Supporting information*).

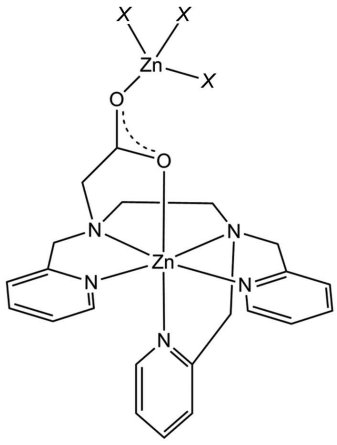
ESI–MS (CH_3CN, 10^{-6} *M*): $[Zn(tpena)]^+$ *m*/*z* 454.121 (calculated: 454.122, $C_{22}H_{24}N_5O_2Zn$) appears in the spectrum of both the chloride and the bromide zinc species. Two peaks are seen for the copper species, *i.e.* one for the isostoichiometric $[Cu(tpena)]^+$ at *m*/*z* 453.119 (453.133, $C_{22}H_{24}CuN_5O_2$) and an additional signal for $[Cu(tpena–CH_2COO–CH_2Py)]^+$ *m*/*z* 317.080 (317.083, $C_{15}H_{18}CuN_4$), for which no analog was observed in the spectra of the zinc complexes.

Analysis found (calculated) (%) for Zn_2(tpena)Cl_3 ($C_{22}H_{24}Cl_3N_5O_2Zn_2$), (I): C 41.89 (42.11), H 3.76 (3.85), N 10.91 (11.16); for Zn_2Br_3(tpena) ($C_{22}H_{24}Br_3N_5O_2Zn_2$), (II): C 35.26 (34.73), H 3.09 (3.18), N 9.19 (9.20); for $[Cu_2Br_3(tpena)][Cu_2Br_3(tpena)(H_2O)]\cdot 6.5H_2O$ ($C_{22}H_{28}Br_3Cu_2N_5O_4$), (III) [which has an overall formula of $Cu_2Br_3(tpena)(H_2O)_{3.75}$, analysed as $Cu_2Br_3(tpena)(H_2O)_2$, indicating some loss of water solvate during drying]: C 33.58 (33.30), H 3.28 (3.55), N 8.72 (8.83).

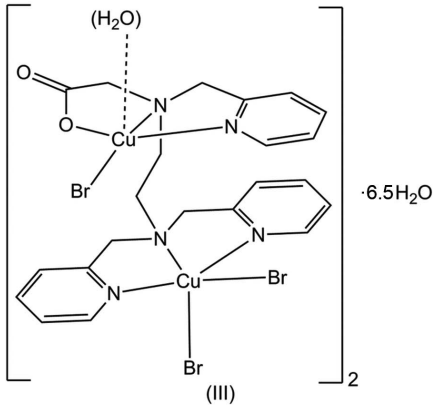
2.2. Refinement

Crystal data, data collection and structure refinement details for Zn_2(tpena)Cl_3, (I), Zn_2Br_3(tpena), (II), and $[Cu_2Br_3(tpena)][Cu_2Br_3(tpena)(H_2O)]\cdot 6.5H_2O$, (III), are summarized in Table 1. Complex (II) was refined as an inversion twin with a Flack (1983) parameter, corresponding with the minor twin fraction, of 0.244 (13). Complex (III) was found to be twinned by a rotation of 180° about reciprocal axis [001].

The data were processed as a two-component twin using *TWINABS* (Sheldrick, 2012) and refined using a data set constructed from all observations involving domain 1, including those that overlapped with observations from domain 2 (*SHELXL* HKLF 5 format). The minor twin fraction was 0.4366 (8). In each structure, all H atoms bonded to C atoms were added in calculated positions, with C—H = 0.99 (CH_2) or 0.95 Å (aromatic) and U_{iso}(H) = 1.2U_{eq}(C). Complex (III) contains hydrogen-bonded water molecules. Most of the



(I) *X* = Cl
(II) *X* = Br



One molecule with coordinated water molecule, one without.

H atoms were not evident in difference maps, but the water O atoms are within hydrogen-bonding distance of each other. Attempts to develop a self-consistent model starting from the acceptors (carbonyl groups and bromide ligands) that could not be hydrogen-bond donors were only partially successful, suggesting that at least some of the H-atom sites may be disordered. These H atoms were not included in the model. One of the water molecules (O12) is disordered about a centre of inversion and was refined with 50% occupancy.

3. Results and discussion

The copper and zinc halides of tpena are prepared easily by direct reaction of the metal salts with Na(tpena) in methanol. Regardless of reaction stoichiometry, *i.e.* a 1:1 or a 1:2 ligand–metal salt reaction, elemental (CHN) analyses suggested that we had not obtained the desired complexes [*M*(tpena)]*X* (*M* = Cu^{2+} or Zn^{2+} and *X* = Br^- or Cl^-), with tpena acting as a straightforward hexadentate ligand for a six-coordinated metal ion. The elemental analyses suggested that all three compounds have the same tpena–*M*–Cl 1:2:3 stoichiometry, while ESI mass spectra recorded in acetonitrile confusingly showed simple $[M(\text{tpena})]^+$ at *m*/*z* 454.121 and 453.119 as the only ion, or a major ion, for the zinc and copper complexes, respectively (Fig. 1). The presence of a dominant $[M(\text{tpena})]^+$ ion in these spectra was entirely comparable to the spectra for the simple Cr^{III} and Co^{III} salts containing the $[M(\text{tpena})]^+$ cation (Vad *et al.*, 2011; de Sousa *et al.*, 2015).

Thus, the usual characterization methods gave no indication of the significant structural differences between the copper

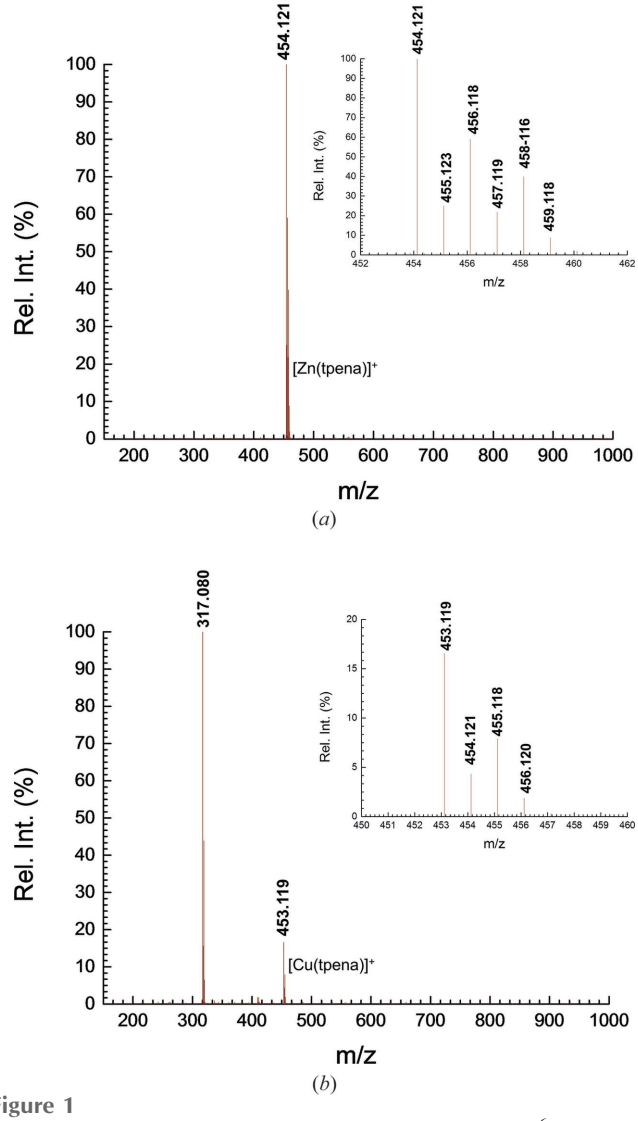


Figure 1
The ESI mass spectra (acetonitrile, positive mode, 10^{-6} *M*) of (*a*) Zn_2Br_3(tpena) and (*b*) Cu_2Br_3(tpena). The ion at *m*/*z* 317.080 in part (*b*) is due to the loss of a CH_2Py arm and CO_2 from [Cu(tpena–CO_2–CH_2Py)]$^+$ (see Fig. 2 for proposed structure).

Table 2
Selected geometric parameters (Å, °) for (I).

Zn1—N1	2.203 (3)	Zn2—O2	1.982 (2)
Zn1—N2	2.061 (3)	Zn2—Cl1	2.2618 (10)
Zn1—N3	2.069 (3)	Zn2—Cl2	2.2511 (9)
Zn1—O1	2.177 (2)	Zn2—Cl3	2.2317 (9)
N2—Zn1—N3	119.85 (10)	N3—Zn1—N1	94.10 (11)
N2—Zn1—O1	87.74 (9)	O1—Zn1—N1	165.91 (9)
N3—Zn1—O1	95.22 (10)	N4—Zn1—N1	78.48 (11)
N2—Zn1—N4	80.25 (10)	N5—Zn1—N1	92.94 (10)
N3—Zn1—N4	159.51 (10)	O2—Zn2—Cl3	111.52 (8)
O1—Zn1—N4	89.19 (9)	O2—Zn2—Cl2	107.91 (8)
N2—Zn1—N5	158.26 (11)	Cl3—Zn2—Cl2	113.68 (4)
N3—Zn1—N5	78.60 (10)	O2—Zn2—Cl1	100.32 (8)
O1—Zn1—N5	78.60 (9)	Cl3—Zn2—Cl1	109.17 (4)
N4—Zn1—N5	82.70 (10)	Cl2—Zn2—Cl1	113.46 (4)
N2—Zn1—N1	96.75 (11)		

and zinc complexes that we have found in the solid state. However, close (and retrospective) inspection of IR spectra reveal small differences in the ν_{as}(OCO) carbonyl stretches just above 1600 cm^{-1}. With the knowledge gained from the crystal structure analyses these are indicative of the *anti*-μ-OCO arrangement of the bridging carboxylate donor in the zinc complexes and the monodendate terminal carboxylate group in the copper complex. Further, the ESI mass spectrum of the copper complex indicates that this complex is more easily fragmented. A prominent daughter ion at *m*/*z* 317.080 is due to decarboxylation and loss of a methylpyridyl arm. A proposed structure for the daughter ion is given in Fig. 2.

Table 3
Selected geometric parameters (Å, °) for (II).

Zn1—N1	2.200 (7)	Zn3—N6	2.207 (6)
Zn1—N2	2.094 (7)	Zn3—N7	2.088 (6)
Zn1—N3	2.080 (7)	Zn3—N8	2.094 (7)
Zn1—N4	2.182 (7)	Zn3—N9	2.183 (7)
Zn1—N5	2.192 (6)	Zn3—N10	2.194 (6)
Zn1—O1	2.184 (5)	Zn3—O3	2.202 (5)
Zn2—O2	2.001 (6)	Zn4—O4	2.008 (6)
Zn2—Br1	2.3721 (13)	Zn4—Br4	2.3816 (12)
Zn2—Br2	2.3953 (12)	Zn4—Br5	2.3856 (12)
Zn2—Br3	2.3776 (12)	Zn4—Br6	2.4161 (11)
N3—Zn1—N2	118.6 (2)	N7—Zn3—N8	118.7 (2)
N3—Zn1—N4	160.0 (2)	N7—Zn3—N9	79.3 (3)
N2—Zn1—N4	80.6 (3)	N8—Zn3—N9	156.9 (3)
N3—Zn1—O1	94.3 (2)	N7—Zn3—N10	160.7 (2)
N2—Zn1—O1	87.2 (2)	N8—Zn3—N10	80.3 (2)
N4—Zn1—O1	92.1 (2)	N9—Zn3—N10	83.5 (3)
N3—Zn1—N5	79.7 (3)	N7—Zn3—O3	95.0 (2)
N2—Zn1—N5	157.6 (3)	N8—Zn3—O3	85.9 (2)
N4—Zn1—N5	83.2 (3)	N9—Zn3—O3	77.8 (3)
O1—Zn1—N5	78.0 (2)	N10—Zn3—O3	89.7 (2)
N3—Zn1—N1	92.2 (2)	N7—Zn3—N6	95.0 (2)
N2—Zn1—N1	97.1 (2)	N8—Zn3—N6	95.9 (2)
N4—Zn1—N1	79.0 (2)	N9—Zn3—N6	96.7 (3)
O1—Zn1—N1	169.4 (2)	N10—Zn3—N6	78.4 (2)
N5—Zn1—N1	94.9 (3)	O3—Zn3—N6	167.5 (2)
O2—Zn2—Br1	109.13 (16)	O4—Zn4—Br4	111.24 (18)
O2—Zn2—Br3	106.34 (17)	O4—Zn4—Br5	107.97 (16)
Br1—Zn2—Br3	114.46 (5)	Br4—Zn4—Br5	114.75 (5)
O2—Zn2—Br2	101.41 (17)	O4—Zn4—Br6	101.45 (17)
Br1—Zn2—Br2	112.24 (5)	Br4—Zn4—Br6	110.00 (4)
Br3—Zn2—Br2	112.20 (5)	Br5—Zn4—Br6	110.60 (5)

Table 4
Selected geometric parameters (Å, °) for (III).

Cu1—N1	1.982 (7)	Cu3—N6	1.998 (7)
Cu1—N2	1.989 (7)	Cu3—N7	1.986 (7)
Cu1—N4	2.133 (6)	Cu3—N9	2.075 (7)
Cu2—O1	1.944 (5)	Cu3—Br4	2.7342 (15)
Cu1—Br2	2.4361 (13)	Cu3—Br5	2.4102 (14)
Cu1—Br1	2.5228 (14)	Cu4—N8	1.955 (7)
Cu2—N3	1.970 (6)	Cu4—N10	2.023 (7)
Cu2—N5	2.046 (6)	Cu4—O3	1.900 (6)
Cu2—O5	2.309 (6)	Cu4—Br6	2.3496 (14)
Cu2—Br3	2.3832 (13)		
N1—Cu1—N2	163.4 (3)	N5—Cu2—Br3	148.96 (19)
N1—Cu1—N4	81.7 (3)	O5—Cu2—Br3	118.76 (16)
N2—Cu1—N4	82.1 (3)	N7—Cu3—N6	164.5 (3)
N1—Cu1—Br2	95.53 (19)	N7—Cu3—N9	82.7 (3)
N2—Cu1—Br2	97.3 (2)	N6—Cu3—N9	82.1 (3)
N4—Cu1—Br2	127.66 (18)	N7—Cu3—Br5	96.3 (2)
N1—Cu1—Br1	90.5 (2)	N6—Cu3—Br5	97.4 (2)
N2—Cu1—Br1	92.5 (2)	N9—Cu3—Br5	141.93 (19)
N4—Cu1—Br1	113.38 (18)	N7—Cu3—Br4	91.0 (2)
Br2—Cu1—Br1	118.91 (5)	N6—Cu3—Br4	88.7 (2)
O1—Cu2—N3	166.6 (2)	N9—Cu3—Br4	99.52 (19)
O1—Cu2—N5	83.8 (2)	Br5—Cu3—Br4	118.54 (5)
N3—Cu2—N5	84.0 (3)	O3—Cu4—N8	156.6 (3)
O1—Cu2—O5	86.6 (2)	O3—Cu4—N10	86.3 (3)
N3—Cu2—O5	88.4 (2)	N8—Cu4—N10	84.2 (3)
N5—Cu2—O5	92.0 (2)	O3—Cu4—Br6	98.34 (19)
O1—Cu2—Br3	93.36 (17)	N8—Cu4—Br6	100.6 (2)
N3—Cu2—Br3	99.98 (19)	N10—Cu4—Br6	149.85 (19)

The complexes crystallized as Zn_2(tpena)Cl_3, (I), Zn_2Br_3-(tpena), (II), and [Cu_2Br_3(tpena)][Cu_2Br_3(tpena)(H_2O)]·-6.5H_2O, (III), all containing neutral complex molecules; selected bond length and angle data are presented in Tables 2–4.

The asymmetric unit of complex (I) comprises one Zn_2(tpena)Cl_3 formula unit (Fig. 3). The Zn1 ion occupies the six-coordinate N_5O site, with irregular geometry imposed by the five five-membered chelate rings. The second metal ion, Zn2, has an approximately tetrahedral Cl_3O coordination sphere, being linked to the tpena ligand through a single coordinate bond to carboxylate atom O2. The carboxylate group acts as an *anti*-1,3-bridge between the two Zn^{II} ions. The pyridine groups in the N_4 plane link the molecules into π-stacked columns generated by the symmetry operations ($-x+1, -y+1, -z+1$) and ($-x+2, -y+1, -z+1$) (Fig. 4), though the interacting rings are not parallel.

The asymmetric unit of complex (II) comprises two independent Zn_2Br_3(tpena) formula units (Fig. 5), each with the

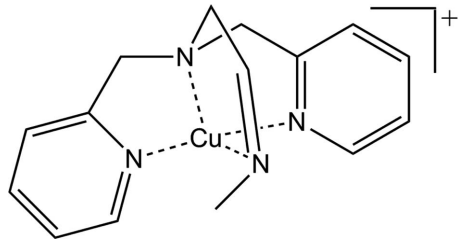


Figure 2
Proposed structure for the daughter ion at *m*/*z* 317.080 in the ESI MS spectrum of Cu_2Br_3(tpena), (II).

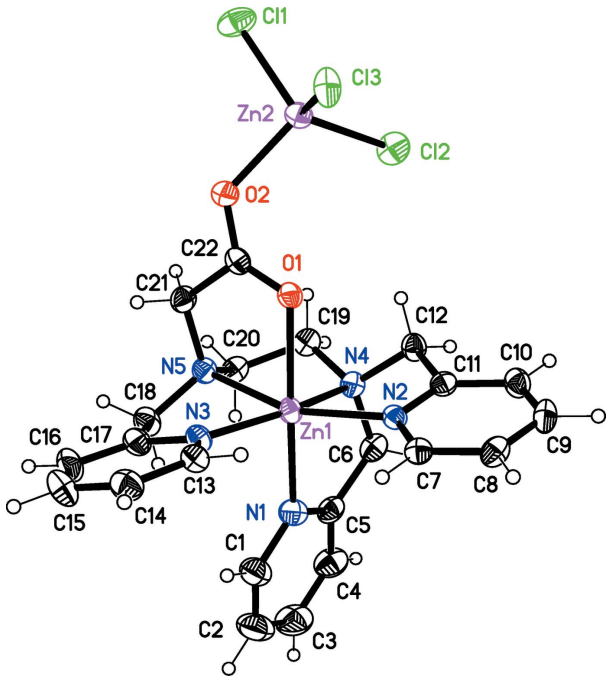


Figure 3
Perspective view of $Zn_2(tpena)Cl_3$, (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of an arbitrary radius.

same connectivity as described for chloride complex (I). The two independent molecules are linked by π-stacking between the pyridine groups in the N_4 planes [centroid–centroid distances = 3.673 (4) and 3.803 (4) Å], but, in contrast to complex (I), the stacking does not extend through the structure. The crystal packing is dominated by a substantal number of C—H···Br hydrogen bonds in the range 3.58–3.94 Å (Table 5).

In copper complex (III), there are two independent molecular units, as shown in Fig. 6. In contrast to complexes (I) and (II), the central ethylenediamine section of the tpena ligand is extended, providing two separate tridentate binding sites, *i.e.* one N_3 and one N_2O. In each molecule, one Cu^{II} ion (Cu1 or Cu3) is in the N_3 site [where the N-atom donors are from the bis(pyridin-2-ylmethyl)amine group at atoms N4 or

Table 5
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···Br4	0.95	3.12	3.700 (8)	121
C6—H6A···Br3^{i}	0.99	3.12	3.724 (8)	121
C6—H6B···Br2^{i}	0.99	2.81	3.710 (8)	152
C12—H12B···Br1	0.99	2.88	3.853 (8)	167
C13—H13···O3	0.95	2.38	3.145 (10)	137
C14—H14···Br5	0.95	3.05	3.939 (9)	157
C15—H15···Br3^{ii}	0.95	2.76	3.578 (8)	145
C18—H18A···Br6^{iii}	0.99	2.85	3.764 (8)	155
C18—H18B···Br1^{iv}	0.99	3.05	3.583 (10)	115
C19—H19B···Br3^{i}	0.99	2.92	3.747 (9)	141
C26—H26···O4^{v}	0.95	2.54	3.381 (11)	148
C28—H28A···Br6^{v}	0.99	2.85	3.762 (8)	154
C29—H29···O1	0.95	2.53	3.334 (9)	142
C34—H34B···Br2^{vi}	0.99	2.77	3.698 (7)	157
C40—H40A···Br5	0.99	2.84	3.801 (8)	165
C42—H42A···Br4^{v}	0.99	3.07	3.900 (8)	142

Symmetry codes: (i) $x+\frac{1}{2}, -y+2, z$; (ii) $-x+\frac{1}{2}, y, z+\frac{1}{2}$; (iii) $x, y+1, z$; (iv) $-x+1, -y+2, z+\frac{1}{2}$; (v) $x-\frac{1}{2}, -y+1, z$; (vi) $x, y-1, z$.

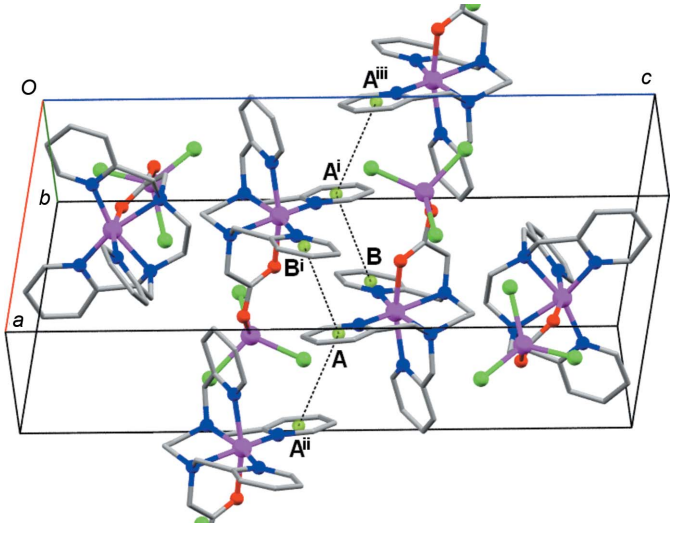


Figure 4
Packing diagram for complex (I), showing π-stacked columns, where **A** and **B** are the centroids of the pyridine rings containing atoms N2 and N3, respectively. The centroid–centroid distances are **A**···**B**^{i} = 3.844 (2) Å and **A**···**A**^{ii} = 3.986 (3) Å. [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$; (iii) $x-1, y, z$.]

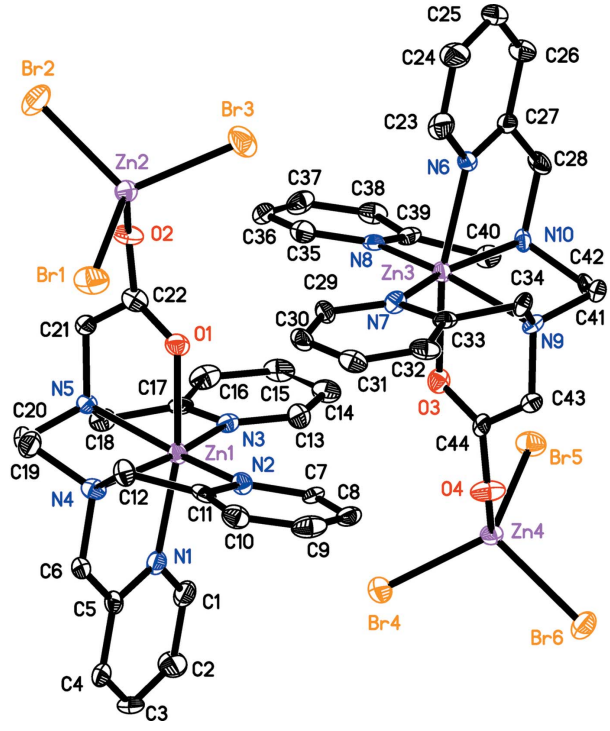


Figure 5
The molecular structure of $Zn_2Br_3(tpena)$, (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

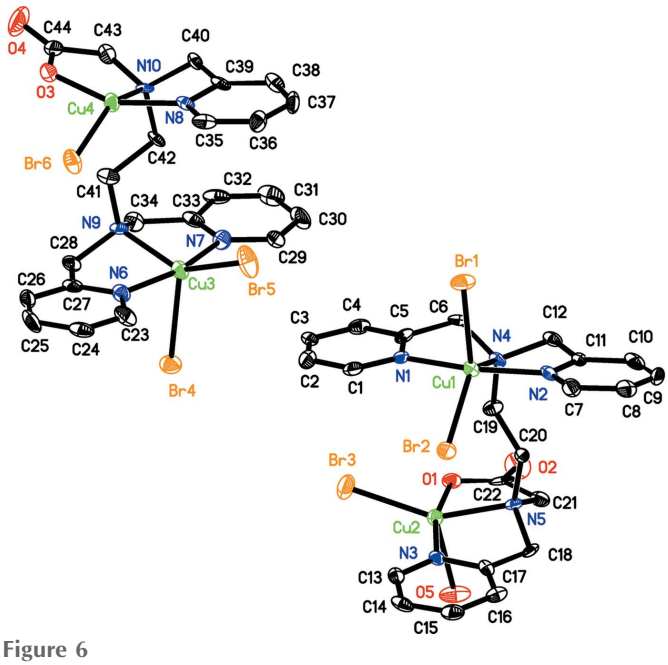


Figure 6
Perspective view of the two independent molecules of (III). Displacement ellipsoids are drawn at the 50% probability level, and H atoms and uncoordinated water molecules have been omitted for clarity.

N9], with two additional bromide ligands. The geometry at these Cu^{II} ions is trigonal bipyramidal, with the pyridine donors axial and with τ values (Addison *et al.*, 1984) of 0.60 and 0.38 for Cu1 and Cu3, respectively. The second Cu^{II} ion in each molecule (Cu2 or Cu4) is bound by the tpena ligand N_2O donor set (amine, pyridine and carboxylate), along with a bromide ion. Atom Cu4 is four-coordinate and approaching square planar [the angle between the N—Cu—N and O—Cu—Br planes is 35.05 (16)°], while atom Cu2 has a coordinated water molecule as the fifth ligand and is closest to square pyramidal (τ = 0.29). There is no convincing π-stacking in

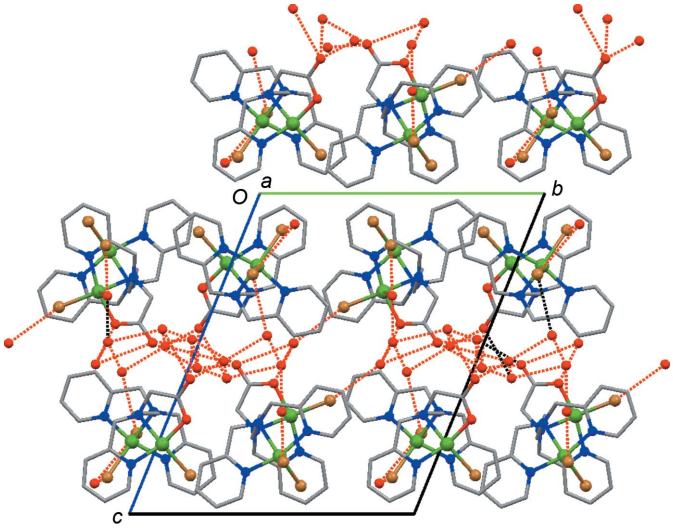


Figure 7
Hydrogen-bonded columns of water molecules parallel to the *a* axis in complex (III).

Table 6
Hydrogen-bond distances (Å) for (III).

Hydrogen bond	*D*···*A*	Hydrogen bond	*D*···*A*
O5···O6^{i}	2.764 (8)	O9···Br4	3.335 (6)
O5···Br1^{ii}	3.199 (6)	O9···O10	2.794 (9)
O6···O8	2.973 (8)	O10···O4^{iii}	2.813 (10)
O6···O9	2.770 (8)	O10···O8	2.885 (10)
O7···O6	2.717 (8)	O11···Br4	3.455 (8)
O7···Br3	3.275 (6)	O11···Br5	3.480 (10)
O8···O4^{ii}	3.052 (10)	O12···O2^{i}	2.575 (14)
O8···O12	2.860 (15)	O12···O2^{iv}	2.834 (13)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $-x+2, -y, -z+1$; (iv) $x, y-1, z$.

complex (III), instead the packing is apparently controlled by hydrogen bonding in columns parallel to the *a* axis, involving the water molecules, the uncoordinated carboxylate O atoms and some of the bromide ions (Table 6 and Fig. 7).

All previously published complexes containing tpena have been ionic species with a 1:1 metal–tpena ratio in which the metal ion binds either all six tpena donors in six or seven-coordinated complexes (Vad *et al.*, 2011; Lennartson & McKenzie, 2012; de Sousa *et al.*, 2015) or releases one pyridine donor to bind an exogenous ligand (Vad *et al.*, 2012; Lennartson & McKenzie, 2012; de Sousa *et al.*, 2015). Carboxylate bridging to another metal ion has also been observed previously in related systems, but in those cases the link has resulted in polynuclear manganese(II) ionic assemblies with all the metal ions in similar environments (Berggren *et al.*, 2009; Egdal *et al.*, 2011). The presence of halides and less oxophilic metal ions has driven the formation of halide complexes and different phases. In the current complexes, the

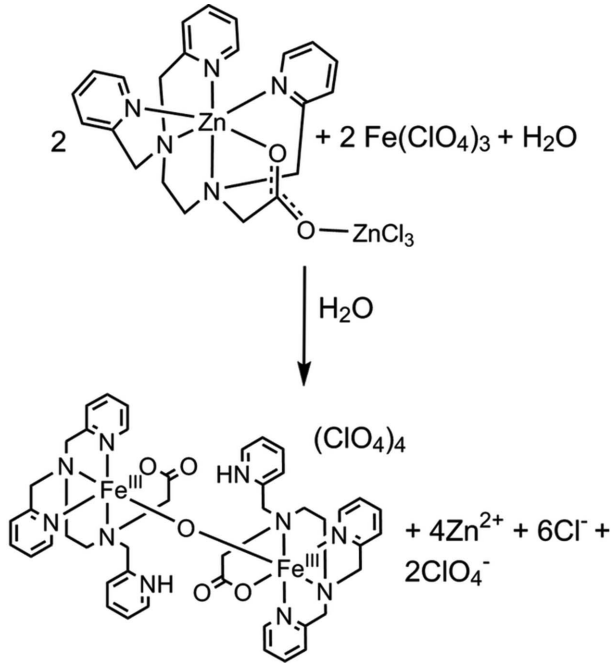


Figure 8
The use of a metathesis reaction for preparing pure samples of an oxide-bridged diiron(III) complex.

2:1 metal–tpena stoichiometry and availability of relatively strongly coordinating halide anions provide the conditions required for the isolation of neutral dinuclear compounds. In zinc complexes (I) and (II), tpena acts as a hexadentate ligand and the encapsulated metal binding site is essentially the same as that reported previously for the mononuclear Co^{III} and Cr^{III} complexes (Vad *et al.*, 2011; de Sousa *et al.*, 2015). The tetrahedral OX_3 coordination of the second zinc ion is quite common (Cambridge Structural Database, Version 5.36; Groom & Allen, 2014). A few examples of *M*–(OCO)–$ZnCl_3$ linkages involving pendant carboxylate groups are known (Panneerselvam, Lu, Chi, Liao & Chung, 2000; Panneerselvam, Lu, Chi, Tung & Chung, 2000; Barfod *et al.*, 2005) and their geometry is similar to that of complex (I); no bromide analogs of (II) were found.

The structure of (III) is unexpected and is perhaps a consequence of the preference of copper(II) for pentacoordination and the difficulty of accommodating a Jahn–Teller ion in the N_5O site. The structure might suggest that the incorporation of stiffening backbones could be advisable when designing catalysts based on ligands of this type if reactivity is dependent on catalytically competent mononuclear metal species.

The separation and purification of polypyridyl ligands, typically from reactions between amines and alkyl halides, in pure forms is often difficult. Sticky brown oils not amenable to chromatography or distillation, containing related ligands, are the standard products. With the introduction of carboxylate groups this problem is only exacerbated since their zwitterionic character introduces considerable separation and purification issues during work-up. The isolation and characterization of Zn_2(tpena)Cl_3 has opened up a significantly improved methodology for the preparation of the pro-catalyst iron complex $[Fe^{III}_2(\mu\text{-O})(\text{tpenaH})_2](ClO_4)_4$ (Lennartson & McKenzie, 2012). If zinc chloride is used in the final stage of ligand synthesis, Zn_2(tpena)Cl_3 can be isolated directly from dirty reaction mixtures without prior separation of tpenaH. A subsequent metathesis reaction in water with the more oxophilic iron(III) results in the clean conversion to $[Fe^{III}_2(\mu\text{-O})(\text{tpenaH})_2](ClO_4)_4$ (Fig. 8). Zinc-doped products can be an issue in reactions like this; however, this is not the case here due to the inherent and metal-specific structural differences, specifically, the requirement of an oxide-bridging group for the diiron(III) complex. It is an elegant metathesis reaction since zinc can simply not form the same oxide-bridged structures as iron. Crystallization is a key, however, and precipitations will yield a powder containing both $[Fe^{III}_2(\mu\text{-O})(\text{tpenaH})_2](ClO_4)_4$ and Zn_2(tpena)Cl_3, as conveniently checked by ESI mass spectrometry. However, if these precipitates are allowed to stand in their mother liquor, over a period of a few days all the metathesis is completed and large crystals of $[Fe^{III}_2(\mu\text{-O})(\text{tpenaH})_2](ClO_4)_4$ are easily recovered.

Acknowledgements

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supporting information

Acta Cryst. (2016). C**72**, 68-74 [doi:10.1107/S2053229615023773]

A coordinatively flexible hexadentate ligand gives structurally isomeric complexes $M_2(L)X_3$ (M = Cu, Zn; X = Br, Cl)

Christina Wegeberg, Vickie McKee and Christine J. McKenzie

Computing details

Data collection: *APEX2* (Bruker, 2012) for II_vcm14089, III_vCM14087twin5. For all compounds, cell refinement: *APEX2* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *SHELXTL* (Bruker, 2012) and *Mercury* (Macrae *et al.*, 2006). Software used to prepare material for publication: *SHELXTL* (Bruker, 2012) and *publCIF* (Westrip, 2010) for I_vCM14088; *publCIF* (Westrip, 2010) for II_vcm14089, III_vCM14087twin5.

(I_vCM14088) Trichlorido[μ-*N*,*N*,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine-*N*′-acetato]dizinc(II)

Crystal data

$[Zn_2(C_{22}H_{24}N_5O_2)Cl_3]$
M_r = 627.55
Monoclinic, $P2_1/n$
a = 9.4985 (8) Å
b = 11.3423 (10) Å
c = 23.3697 (18) Å
β = 98.263 (4)°
V = 2491.6 (4) Å^3
Z = 4
$F(000)$ = 1272
D_x = 1.673 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9964 reflections
θ = 2.5–26.0°
μ = 2.28 mm^{-1}
T = 180 K
Rhomb, colourless
0.31 × 0.19 × 0.15 mm

Data collection

Bruker–Nonius X8 APEXII CCD diffractometer
Radiation source: fine-focus sealed-tube
Detector resolution: 9.1 pixels mm^{-1}
thin–slice ω and φ scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.469, T_{max} = 0.745
77315 measured reflections
5051 independent reflections
4340 reflections with $I > 2\sigma(I)$
R_{int} = 0.084
θ_{max} = 26.5°, θ_{min} = 2.5°
h = −11→11
k = −14→13
l = −29→29

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.099
S = 1.14
5051 reflections
307 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 4.0296P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.66652 (4)	0.59825 (3)	0.60251 (2)	0.02094 (11)
Zn2	0.30820 (4)	0.23885 (3)	0.63634 (2)	0.02351 (12)
Cl1	0.14357 (10)	0.19496 (9)	0.69401 (4)	0.0385 (2)
Cl2	0.52626 (9)	0.16828 (9)	0.66938 (4)	0.0345 (2)
Cl3	0.22696 (9)	0.18402 (8)	0.54590 (4)	0.0324 (2)
N1	0.8417 (3)	0.7254 (3)	0.62309 (12)	0.0279 (6)
C1	0.8453 (4)	0.8372 (3)	0.60389 (16)	0.0345 (8)
H1	0.7708	0.8637	0.5753	0.041*
C2	0.9529 (5)	0.9145 (4)	0.62419 (19)	0.0465 (11)
H2	0.9531	0.9927	0.6096	0.056*
C3	1.0607 (5)	0.8762 (4)	0.66625 (19)	0.0484 (11)
H3	1.1352	0.9282	0.6815	0.058*
C4	1.0586 (4)	0.7627 (4)	0.68558 (17)	0.0382 (9)
H4	1.1319	0.7347	0.7143	0.046*
C5	0.9481 (4)	0.6887 (3)	0.66285 (14)	0.0283 (8)
C6	0.9470 (4)	0.5620 (3)	0.68158 (14)	0.0280 (7)
H6A	1.0138	0.5170	0.6611	0.034*
H6B	0.9825	0.5577	0.7235	0.034*
N2	0.7699 (3)	0.4872 (2)	0.55245 (11)	0.0205 (6)
C7	0.7788 (3)	0.4962 (3)	0.49628 (13)	0.0222 (7)
H7	0.7341	0.5612	0.4754	0.027*
C8	0.8506 (4)	0.4148 (3)	0.46702 (14)	0.0261 (7)
H8	0.8532	0.4227	0.4267	0.031*
C9	0.9181 (4)	0.3222 (3)	0.49781 (15)	0.0290 (8)
H9	0.9692	0.2655	0.4791	0.035*
C10	0.9106 (4)	0.3129 (3)	0.55629 (15)	0.0272 (7)
H10	0.9573	0.2500	0.5782	0.033*
C11	0.8346 (3)	0.3959 (3)	0.58251 (13)	0.0227 (7)
C12	0.8161 (4)	0.3865 (3)	0.64569 (14)	0.0255 (7)
H12A	0.7288	0.3410	0.6493	0.031*
H12B	0.8982	0.3440	0.6672	0.031*
N3	0.5252 (3)	0.7228 (2)	0.56335 (11)	0.0237 (6)
C13	0.4827 (4)	0.7363 (3)	0.50673 (14)	0.0245 (7)
H13	0.5119	0.6799	0.4808	0.029*
C14	0.3984 (4)	0.8289 (3)	0.48440 (16)	0.0318 (8)
H14	0.3717	0.8375	0.4439	0.038*
C15	0.3537 (4)	0.9086 (3)	0.52233 (17)	0.0383 (9)
H15	0.2954	0.9734	0.5083	0.046*
C16	0.3944 (4)	0.8937 (3)	0.58117 (16)	0.0344 (8)

H16	0.3628	0.9474	0.6078	0.041*
C17	0.4803 (4)	0.8010 (3)	0.60065 (15)	0.0273 (7)
C18	0.5345 (4)	0.7817 (3)	0.66431 (14)	0.0285 (8)
H18A	0.6236	0.8267	0.6753	0.034*
H18B	0.4632	0.8106	0.6880	0.034*
N4	0.8056 (3)	0.5049 (2)	0.67066 (11)	0.0227 (6)
C19	0.7306 (4)	0.5083 (3)	0.72180 (13)	0.0262 (7)
H19A	0.7987	0.4909	0.7570	0.031*
H19B	0.6556	0.4470	0.7180	0.031*
C20	0.6636 (4)	0.6291 (3)	0.72779 (13)	0.0261 (7)
H20A	0.6140	0.6299	0.7623	0.031*
H20B	0.7388	0.6902	0.7330	0.031*
N5	0.5612 (3)	0.6555 (2)	0.67545 (11)	0.0232 (6)
C21	0.4267 (4)	0.5897 (3)	0.67386 (14)	0.0256 (7)
H21A	0.3469	0.6421	0.6584	0.031*
H21B	0.4142	0.5685	0.7139	0.031*
C22	0.4185 (3)	0.4788 (3)	0.63779 (13)	0.0221 (7)
O1	0.5077 (2)	0.4605 (2)	0.60434 (9)	0.0226 (5)
O2	0.3147 (3)	0.4129 (2)	0.64417 (10)	0.0296 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0241 (2)	0.0201 (2)	0.01841 (18)	0.00186 (15)	0.00241 (14)	−0.00207 (14)
Zn2	0.0262 (2)	0.0227 (2)	0.02098 (19)	−0.00089 (16)	0.00127 (14)	0.00260 (14)
Cl1	0.0316 (5)	0.0514 (6)	0.0328 (5)	−0.0075 (4)	0.0055 (4)	0.0157 (4)
Cl2	0.0292 (5)	0.0429 (5)	0.0292 (4)	0.0040 (4)	−0.0037 (3)	0.0089 (4)
Cl3	0.0313 (5)	0.0362 (5)	0.0272 (4)	0.0111 (4)	−0.0037 (3)	−0.0084 (3)
N1	0.0342 (17)	0.0266 (16)	0.0237 (14)	−0.0046 (13)	0.0071 (12)	−0.0033 (11)
C1	0.043 (2)	0.028 (2)	0.0338 (19)	−0.0038 (17)	0.0086 (16)	−0.0009 (15)
C2	0.059 (3)	0.030 (2)	0.052 (3)	−0.013 (2)	0.015 (2)	−0.0004 (18)
C3	0.043 (2)	0.048 (3)	0.054 (3)	−0.018 (2)	0.008 (2)	−0.011 (2)
C4	0.032 (2)	0.047 (3)	0.035 (2)	−0.0099 (18)	0.0024 (16)	−0.0059 (17)
C5	0.0273 (18)	0.034 (2)	0.0251 (17)	−0.0026 (15)	0.0095 (13)	−0.0049 (14)
C6	0.0231 (17)	0.037 (2)	0.0238 (16)	−0.0012 (15)	0.0020 (13)	−0.0026 (14)
N2	0.0208 (14)	0.0188 (14)	0.0215 (13)	−0.0005 (11)	0.0024 (10)	−0.0006 (10)
C7	0.0205 (16)	0.0241 (17)	0.0214 (15)	−0.0015 (13)	0.0004 (12)	0.0000 (12)
C8	0.0233 (17)	0.034 (2)	0.0208 (15)	−0.0014 (15)	0.0036 (12)	−0.0045 (13)
C9	0.0252 (18)	0.030 (2)	0.0318 (18)	0.0069 (15)	0.0052 (14)	−0.0071 (14)
C10	0.0250 (18)	0.0248 (18)	0.0309 (18)	0.0046 (14)	0.0006 (13)	0.0008 (14)
C11	0.0200 (16)	0.0246 (17)	0.0231 (15)	−0.0026 (14)	0.0018 (12)	−0.0007 (13)
C12	0.0264 (18)	0.0251 (18)	0.0246 (16)	0.0048 (14)	0.0027 (13)	0.0024 (13)
N3	0.0272 (15)	0.0199 (14)	0.0236 (14)	−0.0001 (12)	0.0026 (11)	−0.0031 (11)
C13	0.0267 (18)	0.0221 (17)	0.0243 (16)	−0.0005 (14)	0.0027 (13)	−0.0002 (13)
C14	0.034 (2)	0.029 (2)	0.0315 (18)	−0.0011 (16)	0.0008 (14)	0.0031 (15)
C15	0.047 (2)	0.024 (2)	0.044 (2)	0.0087 (17)	0.0020 (17)	0.0049 (16)
C16	0.043 (2)	0.0213 (19)	0.041 (2)	0.0065 (16)	0.0109 (16)	−0.0052 (15)
C17	0.0309 (19)	0.0211 (18)	0.0298 (18)	−0.0025 (15)	0.0046 (14)	−0.0052 (13)

C18	0.035 (2)	0.0234 (18)	0.0274 (17)	−0.0002 (15)	0.0052 (14)	−0.0073 (13)
N4	0.0238 (15)	0.0250 (15)	0.0190 (12)	0.0004 (12)	0.0021 (10)	−0.0021 (10)
C19	0.0258 (18)	0.0317 (19)	0.0207 (15)	0.0017 (15)	0.0016 (12)	0.0019 (13)
C20	0.0252 (18)	0.034 (2)	0.0192 (15)	−0.0028 (15)	0.0034 (12)	−0.0044 (13)
N5	0.0247 (14)	0.0223 (15)	0.0226 (13)	−0.0007 (12)	0.0032 (11)	−0.0042 (11)
C21	0.0251 (18)	0.0268 (18)	0.0259 (16)	−0.0014 (14)	0.0066 (13)	−0.0057 (13)
C22	0.0259 (18)	0.0206 (17)	0.0187 (15)	0.0024 (14)	−0.0007 (12)	0.0015 (12)
O1	0.0256 (12)	0.0200 (12)	0.0227 (11)	−0.0004 (10)	0.0049 (9)	−0.0037 (9)
O2	0.0286 (14)	0.0234 (13)	0.0385 (14)	−0.0031 (11)	0.0107 (10)	−0.0035 (10)

Geometric parameters (Å, º)

Zn1—N1	2.203 (3)	C10—H10	0.9500
Zn1—N2	2.061 (3)	C11—C12	1.516 (4)
Zn1—N3	2.069 (3)	C12—N4	1.473 (4)
Zn1—O1	2.177 (2)	C12—H12A	0.9900
Zn1—N4	2.190 (3)	C12—H12B	0.9900
Zn1—N5	2.195 (3)	N3—C13	1.336 (4)
Zn2—O2	1.982 (2)	N3—C17	1.355 (4)
Zn2—Cl1	2.2618 (10)	C13—C14	1.377 (5)
Zn2—Cl2	2.2511 (9)	C13—H13	0.9500
Zn2—Cl3	2.2317 (9)	C14—C15	1.375 (5)
N1—C5	1.338 (5)	C14—H14	0.9500
N1—C1	1.346 (5)	C15—C16	1.384 (5)
C1—C2	1.379 (6)	C15—H15	0.9500
C1—H1	0.9500	C16—C17	1.368 (5)
C2—C3	1.383 (6)	C16—H16	0.9500
C2—H2	0.9500	C17—C18	1.518 (5)
C3—C4	1.366 (6)	C18—N5	1.470 (4)
C3—H3	0.9500	C18—H18A	0.9900
C4—C5	1.388 (5)	C18—H18B	0.9900
C4—H4	0.9500	N4—C19	1.477 (4)
C5—C6	1.502 (5)	C19—C20	1.526 (5)
C6—N4	1.480 (4)	C19—H19A	0.9900
C6—H6A	0.9900	C19—H19B	0.9900
C6—H6B	0.9900	C20—N5	1.480 (4)
N2—C7	1.331 (4)	C20—H20A	0.9900
N2—C11	1.349 (4)	C20—H20B	0.9900
C7—C8	1.385 (5)	N5—C21	1.475 (4)
C7—H7	0.9500	C21—C22	1.511 (4)
C8—C9	1.378 (5)	C21—H21A	0.9900
C8—H8	0.9500	C21—H21B	0.9900
C9—C10	1.383 (5)	C22—O1	1.250 (4)
C9—H9	0.9500	C22—O2	1.263 (4)
C10—C11	1.382 (5)		
N2—Zn1—N3	119.85 (10)	N4—C12—H12A	109.6
N2—Zn1—O1	87.74 (9)	C11—C12—H12A	109.6

N3—Zn1—O1	95.22 (10)	N4—C12—H12B	109.6
N2—Zn1—N4	80.25 (10)	C11—C12—H12B	109.6
N3—Zn1—N4	159.51 (10)	H12A—C12—H12B	108.1
O1—Zn1—N4	89.19 (9)	C13—N3—C17	118.9 (3)
N2—Zn1—N5	158.26 (11)	C13—N3—Zn1	127.0 (2)
N3—Zn1—N5	78.60 (10)	C17—N3—Zn1	114.0 (2)
O1—Zn1—N5	78.60 (9)	N3—C13—C14	122.7 (3)
N4—Zn1—N5	82.70 (10)	N3—C13—H13	118.7
N2—Zn1—N1	96.75 (11)	C14—C13—H13	118.7
N3—Zn1—N1	94.10 (11)	C15—C14—C13	118.3 (3)
O1—Zn1—N1	165.91 (9)	C15—C14—H14	120.9
N4—Zn1—N1	78.48 (11)	C13—C14—H14	120.9
N5—Zn1—N1	92.94 (10)	C14—C15—C16	119.5 (3)
O2—Zn2—Cl3	111.52 (8)	C14—C15—H15	120.3
O2—Zn2—Cl2	107.91 (8)	C16—C15—H15	120.3
Cl3—Zn2—Cl2	113.68 (4)	C17—C16—C15	119.5 (3)
O2—Zn2—Cl1	100.32 (8)	C17—C16—H16	120.3
Cl3—Zn2—Cl1	109.17 (4)	C15—C16—H16	120.3
Cl2—Zn2—Cl1	113.46 (4)	N3—C17—C16	121.1 (3)
C5—N1—C1	118.2 (3)	N3—C17—C18	116.2 (3)
C5—N1—Zn1	114.8 (2)	C16—C17—C18	122.6 (3)
C1—N1—Zn1	126.7 (3)	N5—C18—C17	109.8 (3)
N1—C1—C2	122.5 (4)	N5—C18—H18A	109.7
N1—C1—H1	118.7	C17—C18—H18A	109.7
C2—C1—H1	118.7	N5—C18—H18B	109.7
C1—C2—C3	118.7 (4)	C17—C18—H18B	109.7
C1—C2—H2	120.6	H18A—C18—H18B	108.2
C3—C2—H2	120.6	C12—N4—C19	114.3 (3)
C4—C3—C2	119.1 (4)	C12—N4—C6	110.8 (3)
C4—C3—H3	120.4	C19—N4—C6	112.3 (2)
C2—C3—H3	120.4	C12—N4—Zn1	102.76 (18)
C3—C4—C5	119.3 (4)	C19—N4—Zn1	105.39 (19)
C3—C4—H4	120.3	C6—N4—Zn1	110.6 (2)
C5—C4—H4	120.3	N4—C19—C20	110.7 (3)
N1—C5—C4	122.1 (4)	N4—C19—H19A	109.5
N1—C5—C6	117.7 (3)	C20—C19—H19A	109.5
C4—C5—C6	120.2 (3)	N4—C19—H19B	109.5
N4—C6—C5	114.4 (3)	C20—C19—H19B	109.5
N4—C6—H6A	108.7	H19A—C19—H19B	108.1
C5—C6—H6A	108.7	N5—C20—C19	109.8 (3)
N4—C6—H6B	108.7	N5—C20—H20A	109.7
C5—C6—H6B	108.7	C19—C20—H20A	109.7
H6A—C6—H6B	107.6	N5—C20—H20B	109.7
C7—N2—C11	118.9 (3)	C19—C20—H20B	109.7
C7—N2—Zn1	128.0 (2)	H20A—C20—H20B	108.2
C11—N2—Zn1	113.1 (2)	C18—N5—C21	111.2 (3)
N2—C7—C8	122.8 (3)	C18—N5—C20	114.8 (3)
N2—C7—H7	118.6	C21—N5—C20	112.5 (3)

C8—C7—H7	118.6	C18—N5—Zn1	103.7 (2)
C9—C8—C7	118.4 (3)	C21—N5—Zn1	108.71 (19)
C9—C8—H8	120.8	C20—N5—Zn1	105.24 (19)
C7—C8—H8	120.8	N5—C21—C22	114.2 (3)
C8—C9—C10	119.2 (3)	N5—C21—H21A	108.7
C8—C9—H9	120.4	C22—C21—H21A	108.7
C10—C9—H9	120.4	N5—C21—H21B	108.7
C11—C10—C9	119.3 (3)	C22—C21—H21B	108.7
C11—C10—H10	120.3	H21A—C21—H21B	107.6
C9—C10—H10	120.3	O1—C22—O2	125.9 (3)
N2—C11—C10	121.4 (3)	O1—C22—C21	120.1 (3)
N2—C11—C12	117.0 (3)	O2—C22—C21	113.9 (3)
C10—C11—C12	121.7 (3)	C22—O1—Zn1	115.3 (2)
N4—C12—C11	110.2 (3)	C22—O2—Zn2	126.4 (2)

(II_vcm14089) Tribromido[*μ*-*N*,*N*,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine-*N*′-acetato]dizinc(II)

Crystal data

$[Zn_2Br_3(C_{22}H_{24}N_5O_2)]$
M_r = 760.93
Orthorhombic, $Pca2_1$
a = 18.7061 (12) Å
b = 13.3342 (9) Å
c = 20.4516 (13) Å
V = 5101.3 (6) Å^3
Z = 8
$F(000)$ = 2976
D_x = 1.982 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9941 reflections
θ = 2.7–23.0°
μ = 6.61 mm^{-1}
T = 180 K
Block, colourless
0.17 × 0.08 × 0.05 mm

Data collection

Bruker–Nonius X8 APEXII CCD diffractometer
Radiation source: fine-focus sealed-tube
Detector resolution: 9.1 pixels mm^{-1}
thin–slice ω and φ scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min} = 0.365, T_{max} = 0.431
127653 measured reflections
11284 independent reflections
8558 reflections with $I > 2\sigma(I)$
R_{int} = 0.081
θ_{max} = 28.4°, θ_{min} = 2.2°
h = −24→23
k = −17→17
l = −26→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.078
S = 1.02
11284 reflections
614 parameters
1 restraint
Primary atom site location: dual
Secondary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}
Absolute structure: Refined as an inversion twin.
Absolute structure parameter: 0.245 (12)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.51652 (5)	0.85593 (6)	0.52058 (4)	0.0149 (2)
Zn2	0.32893 (5)	1.05847 (6)	0.35826 (4)	0.0168 (2)
Br1	0.43284 (5)	1.02792 (8)	0.29484 (5)	0.0322 (2)
Br2	0.29001 (5)	1.22925 (6)	0.35104 (5)	0.0332 (2)
Br3	0.23405 (5)	0.94323 (7)	0.33985 (5)	0.0339 (2)
N1	0.6162 (3)	0.8210 (5)	0.5730 (3)	0.0176 (16)
C1	0.6226 (5)	0.7788 (6)	0.6332 (4)	0.023 (2)
H1	0.5806	0.7669	0.6581	0.028*
C2	0.6875 (5)	0.7527 (6)	0.6592 (5)	0.030 (2)
H2	0.6906	0.7239	0.7016	0.035*
C3	0.7479 (5)	0.7692 (6)	0.6225 (5)	0.031 (2)
H3	0.7934	0.7507	0.6392	0.037*
C4	0.7427 (5)	0.8121 (6)	0.5619 (5)	0.022 (2)
H4	0.7842	0.8228	0.5361	0.027*
C5	0.6757 (4)	0.8399 (5)	0.5388 (4)	0.0176 (18)
C6	0.6692 (4)	0.8887 (6)	0.4726 (4)	0.0195 (19)
H6A	0.7013	0.9477	0.4713	0.023*
H6B	0.6861	0.8407	0.4391	0.023*
N2	0.5234 (3)	0.7410 (5)	0.4511 (3)	0.0161 (15)
C7	0.5005 (4)	0.6454 (6)	0.4554 (4)	0.0161 (18)
H7	0.4769	0.6244	0.4942	0.019*
C8	0.5101 (4)	0.5766 (6)	0.4052 (4)	0.022 (2)
H8	0.4927	0.5100	0.4093	0.026*
C9	0.5451 (5)	0.6062 (6)	0.3494 (5)	0.028 (2)
H9	0.5518	0.5606	0.3142	0.033*
C10	0.5704 (4)	0.7030 (6)	0.3452 (5)	0.022 (2)
H10	0.5965	0.7239	0.3078	0.027*
C11	0.5575 (4)	0.7694 (6)	0.3956 (4)	0.0173 (18)
C12	0.5759 (4)	0.8801 (6)	0.3901 (4)	0.0192 (18)
H12A	0.6163	0.8888	0.3594	0.023*
H12B	0.5343	0.9172	0.3725	0.023*
N3	0.4549 (3)	0.8323 (5)	0.6038 (3)	0.0148 (14)
C13	0.4144 (4)	0.7523 (6)	0.6177 (4)	0.022 (2)
H13	0.4148	0.6969	0.5884	0.027*
C14	0.3721 (4)	0.7470 (6)	0.6726 (4)	0.023 (2)
H14	0.3453	0.6882	0.6821	0.027*
C15	0.3696 (4)	0.8285 (6)	0.7133 (4)	0.0218 (19)
H15	0.3393	0.8277	0.7505	0.026*

C16	0.4112 (5)	0.9126 (6)	0.7002 (4)	0.024 (2)
H16	0.4095	0.9695	0.7281	0.029*
C17	0.4554 (4)	0.9119 (6)	0.6457 (4)	0.0164 (18)
C18	0.5059 (6)	0.9957 (6)	0.6296 (5)	0.020 (2)
H18A	0.4895	1.0584	0.6507	0.024*
H18B	0.5542	0.9797	0.6464	0.024*
N4	0.5957 (3)	0.9218 (5)	0.4550 (3)	0.0170 (15)
C19	0.5845 (5)	1.0319 (7)	0.4607 (4)	0.023 (2)
H19A	0.5423	1.0521	0.4345	0.027*
H19B	0.6268	1.0679	0.4435	0.027*
C20	0.5727 (4)	1.0593 (6)	0.5321 (4)	0.0217 (19)
H20A	0.6149	1.0387	0.5581	0.026*
H20B	0.5674	1.1329	0.5362	0.026*
N5	0.5087 (4)	1.0098 (5)	0.5578 (4)	0.0147 (17)
C21	0.4424 (4)	1.0583 (6)	0.5336 (4)	0.0176 (18)
H21A	0.4543	1.1266	0.5182	0.021*
H21B	0.4086	1.0650	0.5705	0.021*
C22	0.4051 (5)	1.0019 (6)	0.4781 (5)	0.017 (2)
O1	0.4279 (3)	0.9160 (4)	0.4632 (3)	0.0194 (13)
O2	0.3538 (3)	1.0478 (4)	0.4532 (3)	0.0214 (13)
Zn3	0.23936 (4)	0.64110 (6)	0.48274 (4)	0.0143 (2)
Zn4	0.42713 (5)	0.44178 (6)	0.65074 (4)	0.0162 (2)
Br4	0.52339 (4)	0.54973 (6)	0.67998 (4)	0.0257 (2)
Br5	0.31994 (4)	0.46711 (7)	0.71173 (4)	0.0252 (2)
Br6	0.46490 (4)	0.26880 (6)	0.65729 (4)	0.0263 (2)
N6	0.1355 (3)	0.6728 (5)	0.4359 (3)	0.0148 (15)
C23	0.1242 (5)	0.7156 (6)	0.3771 (4)	0.025 (2)
H23	0.1642	0.7288	0.3498	0.031*
C24	0.0579 (5)	0.7407 (6)	0.3554 (5)	0.030 (2)
H24	0.0522	0.7676	0.3127	0.036*
C25	−0.0018 (5)	0.7274 (6)	0.3951 (5)	0.028 (2)
H25	−0.0480	0.7481	0.3814	0.034*
C26	0.0092 (5)	0.6825 (7)	0.4555 (4)	0.021 (2)
H26	−0.0298	0.6696	0.4841	0.025*
C27	0.0783 (4)	0.6569 (5)	0.4732 (4)	0.0159 (17)
C28	0.0898 (4)	0.6051 (6)	0.5389 (4)	0.0187 (18)
H28A	0.0720	0.6500	0.5738	0.022*
H28B	0.0603	0.5435	0.5399	0.022*
N7	0.2992 (3)	0.6594 (5)	0.3974 (3)	0.0158 (15)
C29	0.3422 (4)	0.7366 (6)	0.3811 (4)	0.0175 (18)
H29	0.3430	0.7943	0.4083	0.021*
C30	0.3849 (4)	0.7344 (6)	0.3264 (4)	0.0200 (19)
H30	0.4133	0.7910	0.3153	0.024*
C31	0.3863 (4)	0.6482 (6)	0.2871 (4)	0.0204 (19)
H31	0.4174	0.6430	0.2505	0.025*
C32	0.3404 (4)	0.5710 (6)	0.3039 (4)	0.0219 (19)
H32	0.3384	0.5126	0.2773	0.026*
C33	0.2975 (4)	0.5775 (6)	0.3584 (4)	0.0168 (17)

C34	0.2455 (6)	0.4961 (5)	0.3786 (4)	0.015 (2)
H34A	0.1964	0.5142	0.3648	0.018*
H34B	0.2586	0.4318	0.3575	0.018*
N8	0.2348 (3)	0.7597 (5)	0.5497 (3)	0.0157 (15)
C35	0.2587 (4)	0.8531 (6)	0.5418 (4)	0.0203 (19)
H35	0.2797	0.8712	0.5012	0.024*
C36	0.2540 (5)	0.9247 (6)	0.5906 (4)	0.0229 (19)
H36	0.2739	0.9896	0.5846	0.027*
C37	0.2194 (4)	0.8996 (6)	0.6484 (4)	0.0229 (19)
H37	0.2133	0.9485	0.6817	0.027*
C38	0.1945 (4)	0.8047 (6)	0.6572 (5)	0.0215 (19)
H38	0.1703	0.7866	0.6963	0.026*
C39	0.2053 (4)	0.7337 (6)	0.6070 (4)	0.0178 (18)
C40	0.1860 (4)	0.6243 (6)	0.6167 (4)	0.0193 (18)
H40A	0.2276	0.5879	0.6349	0.023*
H40B	0.1462	0.6191	0.6485	0.023*
N9	0.2484 (4)	0.4857 (5)	0.4501 (4)	0.0145 (16)
C41	0.1855 (4)	0.4353 (5)	0.4796 (4)	0.0183 (18)
H41A	0.1920	0.3617	0.4777	0.022*
H41B	0.1420	0.4525	0.4544	0.022*
C42	0.1759 (4)	0.4677 (7)	0.5504 (4)	0.0208 (19)
H42A	0.1344	0.4324	0.5697	0.025*
H42B	0.2190	0.4494	0.5759	0.025*
N10	0.1644 (3)	0.5775 (5)	0.5540 (3)	0.0146 (15)
C44	0.3512 (5)	0.4995 (5)	0.5274 (5)	0.015 (2)
C43	0.3159 (4)	0.4406 (6)	0.4729 (4)	0.0176 (18)
H43A	0.3495	0.4359	0.4356	0.021*
H43B	0.3063	0.3717	0.4885	0.021*
O3	0.3294 (3)	0.5853 (4)	0.5418 (3)	0.0187 (13)
O4	0.4032 (3)	0.4543 (4)	0.5554 (3)	0.0245 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0149 (5)	0.0143 (5)	0.0154 (5)	−0.0011 (4)	0.0003 (4)	−0.0014 (4)
Zn2	0.0171 (5)	0.0170 (5)	0.0162 (5)	0.0004 (4)	−0.0009 (4)	−0.0012 (4)
Br1	0.0265 (5)	0.0433 (5)	0.0267 (5)	0.0071 (5)	0.0106 (4)	0.0044 (5)
Br2	0.0410 (6)	0.0192 (4)	0.0392 (6)	0.0071 (4)	0.0088 (5)	0.0060 (4)
Br3	0.0244 (5)	0.0330 (5)	0.0442 (6)	−0.0057 (4)	−0.0005 (4)	−0.0171 (4)
N1	0.020 (4)	0.013 (3)	0.020 (4)	−0.001 (3)	0.000 (3)	0.000 (3)
C1	0.027 (5)	0.015 (4)	0.027 (5)	0.000 (4)	−0.001 (4)	0.001 (4)
C2	0.027 (5)	0.033 (5)	0.029 (5)	−0.001 (4)	−0.010 (5)	0.014 (5)
C3	0.016 (5)	0.023 (5)	0.053 (6)	0.006 (4)	−0.011 (5)	0.005 (4)
C4	0.020 (5)	0.011 (4)	0.037 (6)	0.000 (4)	0.002 (4)	−0.001 (4)
C5	0.017 (4)	0.012 (4)	0.024 (5)	−0.003 (3)	−0.002 (4)	−0.006 (3)
C6	0.014 (4)	0.015 (4)	0.030 (5)	−0.002 (3)	0.001 (4)	0.001 (4)
N2	0.015 (4)	0.017 (4)	0.016 (4)	−0.001 (3)	0.002 (3)	−0.001 (3)
C7	0.014 (4)	0.012 (4)	0.022 (4)	0.005 (3)	−0.001 (4)	0.003 (3)

C8	0.020 (5)	0.016 (4)	0.030 (5)	0.006 (3)	−0.009 (4)	−0.007 (4)
C9	0.028 (5)	0.034 (5)	0.021 (5)	0.014 (4)	−0.006 (4)	−0.008 (4)
C10	0.019 (5)	0.027 (5)	0.021 (5)	0.001 (4)	−0.002 (4)	−0.004 (4)
C11	0.009 (4)	0.027 (5)	0.016 (4)	−0.001 (3)	−0.003 (3)	0.005 (4)
C12	0.022 (4)	0.021 (4)	0.015 (4)	−0.005 (4)	0.002 (4)	0.000 (3)
N3	0.016 (3)	0.015 (3)	0.014 (4)	0.003 (3)	−0.004 (3)	−0.003 (3)
C13	0.019 (5)	0.021 (5)	0.026 (5)	−0.002 (4)	0.003 (4)	0.003 (4)
C14	0.019 (4)	0.029 (5)	0.019 (5)	0.003 (4)	−0.002 (4)	0.000 (4)
C15	0.018 (4)	0.035 (5)	0.013 (4)	0.006 (4)	0.009 (4)	0.005 (4)
C16	0.031 (5)	0.027 (5)	0.016 (5)	0.008 (4)	−0.007 (4)	−0.004 (4)
C17	0.015 (4)	0.020 (4)	0.014 (4)	0.005 (3)	−0.004 (4)	0.004 (3)
C18	0.023 (5)	0.020 (5)	0.016 (5)	0.003 (3)	−0.006 (5)	−0.005 (3)
N4	0.016 (4)	0.024 (4)	0.012 (3)	0.001 (3)	−0.002 (3)	0.003 (3)
C19	0.027 (5)	0.017 (5)	0.024 (5)	−0.001 (4)	−0.004 (4)	0.003 (4)
C20	0.019 (4)	0.014 (4)	0.032 (5)	−0.005 (4)	−0.002 (4)	−0.003 (4)
N5	0.015 (4)	0.014 (4)	0.015 (4)	0.000 (3)	−0.008 (3)	−0.002 (3)
C21	0.016 (4)	0.014 (4)	0.023 (5)	0.001 (3)	−0.004 (4)	−0.001 (4)
C22	0.018 (5)	0.027 (6)	0.007 (5)	0.000 (3)	−0.001 (4)	0.001 (3)
O1	0.017 (3)	0.020 (3)	0.021 (3)	0.001 (2)	−0.003 (3)	−0.005 (3)
O2	0.016 (3)	0.032 (4)	0.017 (3)	0.006 (3)	−0.003 (3)	−0.001 (3)
Zn3	0.0142 (5)	0.0139 (4)	0.0150 (5)	−0.0012 (4)	0.0002 (4)	0.0006 (4)
Zn4	0.0164 (5)	0.0166 (5)	0.0156 (5)	0.0021 (4)	−0.0021 (4)	−0.0003 (4)
Br4	0.0217 (5)	0.0213 (4)	0.0342 (5)	−0.0025 (3)	−0.0037 (4)	−0.0038 (4)
Br5	0.0210 (5)	0.0323 (5)	0.0223 (5)	0.0037 (4)	0.0039 (4)	0.0021 (4)
Br6	0.0315 (5)	0.0161 (4)	0.0312 (5)	0.0030 (4)	0.0020 (4)	0.0002 (4)
N6	0.013 (4)	0.015 (3)	0.017 (4)	−0.001 (3)	−0.001 (3)	0.003 (3)
C23	0.026 (5)	0.024 (5)	0.026 (5)	0.001 (4)	0.007 (4)	0.011 (4)
C24	0.025 (5)	0.035 (5)	0.030 (6)	0.002 (4)	−0.004 (5)	0.015 (5)
C25	0.016 (5)	0.027 (5)	0.042 (6)	0.001 (4)	−0.007 (4)	0.008 (4)
C26	0.016 (5)	0.026 (5)	0.021 (5)	0.002 (4)	0.001 (4)	0.001 (4)
C27	0.015 (4)	0.013 (4)	0.019 (4)	0.000 (3)	−0.004 (4)	0.000 (3)
C28	0.013 (4)	0.026 (5)	0.017 (4)	−0.004 (3)	0.002 (4)	0.006 (3)
N7	0.019 (4)	0.015 (3)	0.013 (4)	0.002 (3)	0.002 (3)	−0.002 (3)
C29	0.014 (4)	0.018 (4)	0.020 (5)	−0.004 (3)	−0.002 (4)	0.002 (3)
C30	0.014 (4)	0.025 (5)	0.022 (5)	−0.003 (3)	0.001 (4)	0.009 (4)
C31	0.018 (4)	0.032 (5)	0.012 (4)	0.001 (4)	−0.005 (4)	0.001 (4)
C32	0.018 (4)	0.030 (5)	0.018 (5)	0.006 (4)	−0.005 (4)	−0.004 (4)
C33	0.014 (4)	0.017 (4)	0.019 (4)	0.005 (3)	−0.005 (4)	−0.002 (4)
C34	0.022 (5)	0.010 (5)	0.013 (5)	0.000 (3)	0.002 (5)	−0.002 (3)
N8	0.010 (3)	0.019 (4)	0.018 (4)	0.003 (3)	0.001 (3)	0.008 (3)
C35	0.017 (4)	0.025 (5)	0.019 (4)	0.001 (4)	0.001 (4)	0.005 (4)
C36	0.020 (5)	0.014 (4)	0.034 (5)	0.002 (3)	−0.008 (4)	0.002 (4)
C37	0.029 (5)	0.018 (4)	0.022 (5)	0.007 (4)	−0.006 (4)	−0.007 (4)
C38	0.018 (4)	0.029 (5)	0.018 (4)	0.005 (4)	−0.002 (4)	−0.003 (4)
C39	0.016 (4)	0.016 (4)	0.021 (5)	0.006 (3)	−0.002 (4)	−0.001 (4)
C40	0.020 (4)	0.022 (4)	0.015 (4)	0.004 (4)	0.003 (4)	0.002 (3)
N9	0.018 (4)	0.012 (3)	0.014 (4)	0.004 (3)	−0.001 (3)	0.001 (3)
C41	0.018 (4)	0.011 (4)	0.026 (5)	−0.001 (3)	−0.003 (4)	0.001 (4)

C42	0.014 (4)	0.020 (5)	0.029 (5)	−0.008 (4)	−0.001 (4)	0.006 (4)
N10	0.016 (4)	0.013 (4)	0.016 (4)	−0.005 (3)	−0.001 (3)	0.002 (3)
C44	0.017 (5)	0.012 (5)	0.015 (5)	−0.001 (3)	0.008 (4)	0.006 (3)
C43	0.016 (4)	0.014 (4)	0.023 (5)	0.002 (3)	−0.001 (4)	0.000 (4)
O3	0.022 (3)	0.017 (3)	0.017 (3)	−0.002 (2)	−0.003 (3)	−0.003 (2)
O4	0.025 (3)	0.033 (4)	0.015 (3)	0.013 (3)	−0.007 (3)	−0.008 (3)

Geometric parameters (Å, º)

Zn1—N1	2.200 (7)	Zn3—N6	2.207 (6)
Zn1—N2	2.094 (7)	Zn3—N7	2.088 (6)
Zn1—N3	2.080 (7)	Zn3—N8	2.094 (7)
Zn1—N4	2.182 (7)	Zn3—N9	2.183 (7)
Zn1—N5	2.192 (6)	Zn3—N10	2.194 (6)
Zn1—O1	2.184 (5)	Zn3—O3	2.202 (5)
Zn2—O2	2.001 (6)	Zn4—O4	2.008 (6)
Zn2—Br1	2.3721 (13)	Zn4—Br4	2.3816 (12)
Zn2—Br2	2.3953 (12)	Zn4—Br5	2.3856 (12)
Zn2—Br3	2.3776 (12)	Zn4—Br6	2.4161 (11)
N1—C5	1.339 (10)	N6—C27	1.332 (10)
N1—C1	1.359 (10)	N6—C23	1.347 (10)
C1—C2	1.370 (12)	C23—C24	1.360 (12)
C1—H1	0.9500	C23—H23	0.9500
C2—C3	1.375 (13)	C24—C25	1.391 (13)
C2—H2	0.9500	C24—H24	0.9500
C3—C4	1.368 (12)	C25—C26	1.389 (13)
C3—H3	0.9500	C25—H25	0.9500
C4—C5	1.390 (11)	C26—C27	1.384 (11)
C4—H4	0.9500	C26—H26	0.9500
C5—C6	1.507 (11)	C27—C28	1.524 (11)
C6—N4	1.489 (10)	C28—N10	1.476 (10)
C6—H6A	0.9900	C28—H28A	0.9900
C6—H6B	0.9900	C28—H28B	0.9900
N2—C7	1.347 (9)	N7—C29	1.348 (9)
N2—C11	1.356 (10)	N7—C33	1.352 (9)
C7—C8	1.390 (11)	C29—C30	1.374 (11)
C7—H7	0.9500	C29—H29	0.9500
C8—C9	1.374 (13)	C30—C31	1.404 (11)
C8—H8	0.9500	C30—H30	0.9500
C9—C10	1.377 (12)	C31—C32	1.384 (12)
C9—H9	0.9500	C31—H31	0.9500
C10—C11	1.380 (11)	C32—C33	1.377 (11)
C10—H10	0.9500	C32—H32	0.9500
C11—C12	1.520 (11)	C33—C34	1.516 (11)
C12—N4	1.485 (10)	C34—N9	1.469 (11)
C12—H12A	0.9900	C34—H34A	0.9900
C12—H12B	0.9900	C34—H34B	0.9900
N3—C13	1.340 (10)	N8—C35	1.334 (10)

N3—C17	1.363 (10)	N8—C39	1.341 (10)
C13—C14	1.375 (11)	C35—C36	1.383 (12)
C13—H13	0.9500	C35—H35	0.9500
C14—C15	1.370 (11)	C36—C37	1.389 (12)
C14—H14	0.9500	C36—H36	0.9500
C15—C16	1.392 (12)	C37—C38	1.361 (11)
C15—H15	0.9500	C37—H37	0.9500
C16—C17	1.387 (11)	C38—C39	1.410 (11)
C16—H16	0.9500	C38—H38	0.9500
C17—C18	1.500 (12)	C39—C40	1.516 (11)
C18—N5	1.482 (12)	C40—N10	1.483 (10)
C18—H18A	0.9900	C40—H40A	0.9900
C18—H18B	0.9900	C40—H40B	0.9900
N4—C19	1.487 (10)	N9—C43	1.475 (11)
C19—C20	1.522 (12)	N9—C41	1.484 (11)
C19—H19A	0.9900	C41—C42	1.522 (12)
C19—H19B	0.9900	C41—H41A	0.9900
C20—N5	1.465 (11)	C41—H41B	0.9900
C20—H20A	0.9900	C42—N10	1.482 (10)
C20—H20B	0.9900	C42—H42A	0.9900
N5—C21	1.484 (11)	C42—H42B	0.9900
C21—C22	1.530 (12)	C44—O3	1.249 (9)
C21—H21A	0.9900	C44—O4	1.279 (10)
C21—H21B	0.9900	C44—C43	1.515 (12)
C22—O2	1.247 (10)	C43—H43A	0.9900
C22—O1	1.259 (9)	C43—H43B	0.9900

N3—Zn1—N2	118.6 (2)	N7—Zn3—N8	118.7 (2)
N3—Zn1—N4	160.0 (2)	N7—Zn3—N9	79.3 (3)
N2—Zn1—N4	80.6 (3)	N8—Zn3—N9	156.9 (3)
N3—Zn1—O1	94.3 (2)	N7—Zn3—N10	160.7 (2)
N2—Zn1—O1	87.2 (2)	N8—Zn3—N10	80.3 (2)
N4—Zn1—O1	92.1 (2)	N9—Zn3—N10	83.5 (3)
N3—Zn1—N5	79.7 (3)	N7—Zn3—O3	95.0 (2)
N2—Zn1—N5	157.6 (3)	N8—Zn3—O3	85.9 (2)
N4—Zn1—N5	83.2 (3)	N9—Zn3—O3	77.8 (3)
O1—Zn1—N5	78.0 (2)	N10—Zn3—O3	89.7 (2)
N3—Zn1—N1	92.2 (2)	N7—Zn3—N6	95.0 (2)
N2—Zn1—N1	97.1 (2)	N8—Zn3—N6	95.9 (2)
N4—Zn1—N1	79.0 (2)	N9—Zn3—N6	96.7 (3)
O1—Zn1—N1	169.4 (2)	N10—Zn3—N6	78.4 (2)
N5—Zn1—N1	94.9 (3)	O3—Zn3—N6	167.5 (2)
O2—Zn2—Br1	109.13 (16)	O4—Zn4—Br4	111.24 (18)
O2—Zn2—Br3	106.34 (17)	O4—Zn4—Br5	107.97 (16)
Br1—Zn2—Br3	114.46 (5)	Br4—Zn4—Br5	114.75 (5)
O2—Zn2—Br2	101.41 (17)	O4—Zn4—Br6	101.45 (17)
Br1—Zn2—Br2	112.24 (5)	Br4—Zn4—Br6	110.00 (4)
Br3—Zn2—Br2	112.20 (5)	Br5—Zn4—Br6	110.60 (5)

C5—N1—C1	118.5 (7)	C27—N6—C23	116.9 (7)
C5—N1—Zn1	114.2 (5)	C27—N6—Zn3	115.4 (5)
C1—N1—Zn1	127.2 (6)	C23—N6—Zn3	127.3 (6)
N1—C1—C2	122.4 (9)	N6—C23—C24	122.6 (8)
N1—C1—H1	118.8	N6—C23—H23	118.7
C2—C1—H1	118.8	C24—C23—H23	118.7
C1—C2—C3	118.4 (9)	C23—C24—C25	120.6 (9)
C1—C2—H2	120.8	C23—C24—H24	119.7
C3—C2—H2	120.8	C25—C24—H24	119.7
C4—C3—C2	120.2 (9)	C26—C25—C24	117.1 (8)
C4—C3—H3	119.9	C26—C25—H25	121.4
C2—C3—H3	119.9	C24—C25—H25	121.4
C3—C4—C5	119.0 (8)	C27—C26—C25	118.5 (9)
C3—C4—H4	120.5	C27—C26—H26	120.7
C5—C4—H4	120.5	C25—C26—H26	120.7
N1—C5—C4	121.5 (7)	N6—C27—C26	124.1 (7)
N1—C5—C6	118.9 (7)	N6—C27—C28	117.6 (7)
C4—C5—C6	119.6 (7)	C26—C27—C28	118.3 (7)
N4—C6—C5	114.8 (7)	N10—C28—C27	115.5 (6)
N4—C6—H6A	108.6	N10—C28—H28A	108.4
C5—C6—H6A	108.6	C27—C28—H28A	108.4
N4—C6—H6B	108.6	N10—C28—H28B	108.4
C5—C6—H6B	108.6	C27—C28—H28B	108.4
H6A—C6—H6B	107.5	H28A—C28—H28B	107.5
C7—N2—C11	117.9 (7)	C29—N7—C33	119.0 (7)
C7—N2—Zn1	128.9 (6)	C29—N7—Zn3	128.0 (5)
C11—N2—Zn1	113.1 (5)	C33—N7—Zn3	112.7 (5)
N2—C7—C8	122.3 (8)	N7—C29—C30	122.1 (7)
N2—C7—H7	118.8	N7—C29—H29	118.9
C8—C7—H7	118.8	C30—C29—H29	118.9
C9—C8—C7	119.1 (8)	C29—C30—C31	119.6 (7)
C9—C8—H8	120.4	C29—C30—H30	120.2
C7—C8—H8	120.4	C31—C30—H30	120.2
C8—C9—C10	118.9 (8)	C32—C31—C30	117.1 (8)
C8—C9—H9	120.5	C32—C31—H31	121.5
C10—C9—H9	120.5	C30—C31—H31	121.5
C9—C10—C11	119.7 (9)	C33—C32—C31	121.0 (8)
C9—C10—H10	120.2	C33—C32—H32	119.5
C11—C10—H10	120.2	C31—C32—H32	119.5
N2—C11—C10	121.9 (8)	N7—C33—C32	121.0 (7)
N2—C11—C12	116.0 (7)	N7—C33—C34	115.7 (7)
C10—C11—C12	121.9 (7)	C32—C33—C34	123.3 (7)
N4—C12—C11	110.8 (7)	N9—C34—C33	108.3 (7)
N4—C12—H12A	109.5	N9—C34—H34A	110.0
C11—C12—H12A	109.5	C33—C34—H34A	110.0
N4—C12—H12B	109.5	N9—C34—H34B	110.0
C11—C12—H12B	109.5	C33—C34—H34B	110.0
H12A—C12—H12B	108.1	H34A—C34—H34B	108.4

C13—N3—C17	119.4 (7)	C35—N8—C39	119.0 (7)
C13—N3—Zn1	127.4 (5)	C35—N8—Zn3	127.8 (6)
C17—N3—Zn1	113.1 (5)	C39—N8—Zn3	113.2 (5)
N3—C13—C14	122.6 (8)	N8—C35—C36	122.5 (8)
N3—C13—H13	118.7	N8—C35—H35	118.8
C14—C13—H13	118.7	C36—C35—H35	118.8
C15—C14—C13	118.3 (8)	C35—C36—C37	118.5 (7)
C15—C14—H14	120.8	C35—C36—H36	120.8
C13—C14—H14	120.8	C37—C36—H36	120.8
C14—C15—C16	120.3 (8)	C38—C37—C36	119.8 (8)
C14—C15—H15	119.9	C38—C37—H37	120.1
C16—C15—H15	119.9	C36—C37—H37	120.1
C17—C16—C15	118.8 (8)	C37—C38—C39	118.6 (8)
C17—C16—H16	120.6	C37—C38—H38	120.7
C15—C16—H16	120.6	C39—C38—H38	120.7
N3—C17—C16	120.4 (7)	N8—C39—C38	121.5 (7)
N3—C17—C18	116.5 (7)	N8—C39—C40	117.4 (7)
C16—C17—C18	123.1 (7)	C38—C39—C40	121.1 (7)
N5—C18—C17	109.6 (7)	N10—C40—C39	110.9 (6)
N5—C18—H18A	109.8	N10—C40—H40A	109.5
C17—C18—H18A	109.8	C39—C40—H40A	109.5
N5—C18—H18B	109.8	N10—C40—H40B	109.5
C17—C18—H18B	109.8	C39—C40—H40B	109.5
H18A—C18—H18B	108.2	H40A—C40—H40B	108.1
C12—N4—C19	113.9 (6)	C34—N9—C43	112.7 (7)
C12—N4—C6	109.6 (6)	C34—N9—C41	114.7 (7)
C19—N4—C6	113.8 (6)	C43—N9—C41	111.5 (6)
C12—N4—Zn1	103.2 (5)	C34—N9—Zn3	102.2 (4)
C19—N4—Zn1	104.7 (5)	C43—N9—Zn3	110.9 (5)
C6—N4—Zn1	111.0 (5)	C41—N9—Zn3	104.1 (5)
N4—C19—C20	109.4 (7)	N9—C41—C42	110.6 (6)
N4—C19—H19A	109.8	N9—C41—H41A	109.5
C20—C19—H19A	109.8	C42—C41—H41A	109.5
N4—C19—H19B	109.8	N9—C41—H41B	109.5
C20—C19—H19B	109.8	C42—C41—H41B	109.5
H19A—C19—H19B	108.2	H41A—C41—H41B	108.1
N5—C20—C19	110.7 (7)	N10—C42—C41	110.1 (7)
N5—C20—H20A	109.5	N10—C42—H42A	109.6
C19—C20—H20A	109.5	C41—C42—H42A	109.6
N5—C20—H20B	109.5	N10—C42—H42B	109.6
C19—C20—H20B	109.5	C41—C42—H42B	109.6
H20A—C20—H20B	108.1	H42A—C42—H42B	108.1
C20—N5—C18	116.2 (7)	C28—N10—C42	111.9 (6)
C20—N5—C21	111.5 (6)	C28—N10—C40	109.6 (6)
C18—N5—C21	110.8 (7)	C42—N10—C40	114.7 (6)
C20—N5—Zn1	104.1 (5)	C28—N10—Zn3	111.6 (5)
C18—N5—Zn1	103.2 (4)	C42—N10—Zn3	104.8 (5)
C21—N5—Zn1	110.3 (5)	C40—N10—Zn3	103.8 (4)

N5—C21—C22	114.5 (6)	O3—C44—O4	125.1 (9)
N5—C21—H21A	108.6	O3—C44—C43	120.4 (8)
C22—C21—H21A	108.6	O4—C44—C43	114.6 (7)
N5—C21—H21B	108.6	N9—C43—C44	113.3 (6)
C22—C21—H21B	108.6	N9—C43—H43A	108.9
H21A—C21—H21B	107.6	C44—C43—H43A	108.9
O2—C22—O1	127.5 (8)	N9—C43—H43B	108.9
O2—C22—C21	114.4 (7)	C44—C43—H43B	108.9
O1—C22—C21	118.1 (8)	H43A—C43—H43B	107.7
C22—O1—Zn1	117.5 (6)	C44—O3—Zn3	115.5 (6)
C22—O2—Zn2	127.6 (6)	C44—O4—Zn4	130.0 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···Br4	0.95	3.12	3.700 (8)	121
C6—H6*A*···Br3^{i}	0.99	3.12	3.724 (8)	121
C6—H6*B*···Br2^{i}	0.99	2.81	3.710 (8)	152
C12—H12*B*···Br1	0.99	2.88	3.853 (8)	167
C13—H13···O3	0.95	2.38	3.145 (10)	137
C14—H14···Br5	0.95	3.05	3.939 (9)	157
C15—H15···Br3^{ii}	0.95	2.76	3.578 (8)	145
C18—H18*A*···Br6^{iii}	0.99	2.85	3.764 (8)	155
C18—H18*B*···Br1^{iv}	0.99	3.05	3.583 (10)	115
C19—H19*B*···Br3^{i}	0.99	2.92	3.747 (9)	141
C26—H26···O4^{v}	0.95	2.54	3.381 (11)	148
C28—H28*A*···Br6^{v}	0.99	2.85	3.762 (8)	154
C29—H29···O1	0.95	2.53	3.334 (9)	142
C34—H34*B*···Br2^{ii}	0.99	2.77	3.698 (7)	157
C40—H40*A*···Br5	0.99	2.84	3.801 (8)	165
C42—H42*A*···Br4^{v}	0.99	3.07	3.900 (8)	142

Symmetry codes: (i) *x*+1/2, −*y*+2, *z*; (ii) *x*, *y*−1, *z*; (iii) *x*, *y*+1, *z*; (iv) −*x*+1, −*y*+2, *z*+1/2; (v) *x*−1/2, −*y*+1, *z*.

(III_vCM14087twin5) Aquatribromido[*μ*-*N*,*N*,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine-*N*′-acetato]dicopper(II)–tribromido[*μ*-*N*,*N*,*N*′-tris(pyridin-2-ylmethyl)ethylenediamine-*N*′-acetato]dicopper(II)–water (1/1/6.5)

Crystal data

$[Cu_2Br_3(C_{22}H_{24}N_5O_2)][Cu_2Br_3(C_{22}H_{24}N_5O_2)(H_2O)]\cdot 6.5H_2O$
M_r = 1649.66
Triclinic, $P\overline{1}$
a = 11.2516 (9) Å
b = 15.0606 (10) Å
c = 18.3213 (14) Å
α = 112.087 (3)°
β = 94.380 (3)°
γ = 90.486 (3)°
V = 2866.1 (4) Å^3
Z = 2
F(000) = 1630
D_x = 1.912 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 7803 reflections
θ = 2.4–26.2°
μ = 5.71 mm^{-1}
T = 180 K
Needle, pale blue
0.20 × 0.11 × 0.05 mm

Data collection

Bruker–Nonius X8 APEXII CCD diffractometer
Radiation source: fine-focus sealed-tube
Detector resolution: 9.1 pixels mm^{-1}
thin–slice ω and φ scans
Absorption correction: multi-scan (TWINABS; Sheldrick, 2012)
T_{min} = 0.303, T_{max} = 0.430
11068 measured reflections
11068 independent reflections
7261 reflections with $I > 2\sigma(I)$
R_{int} = 0.077
θ_{max} = 26.4°, θ_{min} = 2.1°
h = −14→13
k = −18→17
l = 0→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.114
S = 1.00
11068 reflections
686 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.99 e Å^{-3}
$\Delta\rho_{min}$ = −0.88 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component twin.H atoms of the water molecules were not located and are not included in the model.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.40326 (9)	0.55531 (7)	0.18085 (6)	0.0173 (2)	
Cu2	−0.00160 (9)	0.57391 (7)	0.30625 (6)	0.0177 (2)	
Br1	0.62240 (8)	0.53381 (7)	0.16191 (6)	0.0290 (2)	
Br2	0.25880 (9)	0.43804 (6)	0.08770 (5)	0.0256 (2)	
Br3	0.07600 (9)	0.45736 (7)	0.35413 (6)	0.0337 (3)	
N1	0.4155 (6)	0.4927 (4)	0.2587 (4)	0.0172 (16)	
C1	0.4096 (7)	0.3982 (6)	0.2432 (6)	0.027 (2)	
H1	0.3994	0.3541	0.1899	0.032*	
C2	0.4181 (8)	0.3639 (6)	0.3029 (5)	0.026 (2)	
H2	0.4154	0.2967	0.2905	0.031*	
C3	0.4306 (8)	0.4261 (7)	0.3804 (6)	0.033 (3)	
H3	0.4349	0.4026	0.4219	0.040*	
C4	0.4368 (7)	0.5242 (6)	0.3974 (5)	0.021 (2)	
H4	0.4453	0.5692	0.4504	0.026*	
C5	0.4302 (7)	0.5545 (6)	0.3340 (5)	0.017 (2)	
C6	0.4458 (7)	0.6589 (6)	0.3450 (5)	0.018 (2)	
H6A	0.4237	0.7006	0.3980	0.022*	
H6B	0.5302	0.6741	0.3409	0.022*	

N2	0.3931 (6)	0.6521 (4)	0.1311 (4)	0.0206 (17)
C7	0.3885 (8)	0.6315 (6)	0.0521 (5)	0.024 (2)
H7	0.3887	0.5666	0.0163	0.028*
C8	0.3836 (8)	0.7044 (7)	0.0230 (5)	0.026 (2)
H8	0.3831	0.6898	−0.0322	0.031*
C9	0.3794 (7)	0.7961 (6)	0.0738 (5)	0.024 (2)
H9	0.3729	0.8462	0.0543	0.029*
C10	0.3846 (7)	0.8171 (6)	0.1534 (5)	0.023 (2)
H10	0.3822	0.8817	0.1894	0.027*
C11	0.3934 (7)	0.7424 (6)	0.1817 (5)	0.017 (2)
C12	0.4091 (7)	0.7620 (6)	0.2687 (5)	0.018 (2)
H12A	0.4942	0.7779	0.2881	0.022*
H12B	0.3622	0.8176	0.2978	0.022*
N3	−0.0465 (6)	0.4914 (4)	0.1950 (4)	0.0139 (16)
C13	−0.0614 (7)	0.3968 (6)	0.1625 (5)	0.020 (2)
H13	−0.0500	0.3615	0.1957	0.024*
C14	−0.0924 (7)	0.3465 (6)	0.0828 (5)	0.023 (2)
H14	−0.1036	0.2787	0.0620	0.027*
C15	−0.1066 (8)	0.3972 (6)	0.0350 (6)	0.025 (2)
H15	−0.1264	0.3645	−0.0202	0.030*
C16	−0.0918 (7)	0.4979 (6)	0.0672 (5)	0.019 (2)
H16	−0.1010	0.5345	0.0349	0.023*
C17	−0.0633 (7)	0.5415 (5)	0.1482 (5)	0.0138 (19)
C18	−0.0544 (7)	0.6486 (6)	0.1890 (5)	0.0166 (19)
H18A	−0.0254	0.6774	0.1529	0.020*
H18B	−0.1343	0.6731	0.2032	0.020*
N4	0.3688 (6)	0.6764 (4)	0.2834 (4)	0.0154 (16)
C19	0.2442 (7)	0.6811 (6)	0.3058 (5)	0.019 (2)
H19A	0.2357	0.7414	0.3517	0.023*
H19B	0.2266	0.6268	0.3218	0.023*
C20	0.1540 (7)	0.6772 (6)	0.2375 (5)	0.0160 (19)
H20A	0.1680	0.7336	0.2234	0.019*
H20B	0.1648	0.6187	0.1905	0.019*
N5	0.0282 (6)	0.6766 (4)	0.2611 (4)	0.0157 (16)
C21	0.0019 (8)	0.7690 (6)	0.3243 (5)	0.021 (2)
H21A	−0.0816	0.7850	0.3150	0.025*
H21B	0.0550	0.8208	0.3226	0.025*
C22	0.0199 (7)	0.7629 (7)	0.4043 (5)	0.023 (2)
O1	0.0330 (5)	0.6793 (4)	0.4075 (3)	0.0194 (13)
O2	0.0222 (6)	0.8370 (4)	0.4656 (4)	0.0398 (18)
Cu3	0.70717 (10)	0.09427 (7)	0.22562 (6)	0.0212 (3)
Cu4	1.13409 (10)	−0.01614 (7)	0.21751 (6)	0.0203 (3)
Br4	0.47160 (8)	0.09019 (6)	0.25193 (6)	0.0282 (2)
Br5	0.75962 (11)	0.13000 (7)	0.11421 (6)	0.0422 (3)
Br6	1.04997 (9)	−0.15919 (6)	0.12065 (6)	0.0312 (2)
N6	0.6954 (6)	−0.0484 (5)	0.1715 (4)	0.0221 (17)
C23	0.6770 (8)	−0.0997 (6)	0.0939 (6)	0.029 (2)
H23	0.6677	−0.0671	0.0584	0.035*

C24	0.6709 (8)	−0.1985 (6)	0.0638 (5)	0.027 (2)
H24	0.6598	−0.2335	0.0084	0.032*
C25	0.6813 (8)	−0.2461 (6)	0.1149 (6)	0.034 (3)
H25	0.6769	−0.3142	0.0956	0.040*
C26	0.6983 (8)	−0.1920 (6)	0.1953 (6)	0.027 (2)
H26	0.7056	−0.2229	0.2320	0.032*
C27	0.7044 (7)	−0.0942 (6)	0.2219 (5)	0.020 (2)
C28	0.7169 (8)	−0.0307 (6)	0.3085 (5)	0.023 (2)
H28A	0.6370	−0.0169	0.3284	0.027*
H28B	0.7617	−0.0635	0.3390	0.027*
N7	0.7297 (6)	0.2275 (5)	0.3049 (4)	0.0227 (17)
C29	0.7216 (8)	0.3103 (6)	0.2910 (6)	0.026 (2)
H29	0.7055	0.3064	0.2382	0.031*
C30	0.7361 (8)	0.3986 (6)	0.3508 (6)	0.033 (3)
H30	0.7288	0.4549	0.3394	0.040*
C31	0.7617 (9)	0.4058 (7)	0.4281 (6)	0.036 (3)
H31	0.7733	0.4668	0.4699	0.043*
C32	0.7698 (8)	0.3229 (6)	0.4433 (6)	0.029 (2)
H32	0.7872	0.3255	0.4957	0.034*
C33	0.7519 (8)	0.2354 (6)	0.3800 (5)	0.022 (2)
C34	0.7577 (8)	0.1416 (6)	0.3937 (5)	0.024 (2)
H34A	0.8218	0.1472	0.4355	0.029*
H34B	0.6811	0.1282	0.4116	0.029*
N8	1.1389 (6)	0.0651 (4)	0.1559 (4)	0.0178 (16)
C35	1.1268 (7)	0.0387 (6)	0.0774 (5)	0.025 (2)
H35	1.1173	−0.0276	0.0452	0.030*
C36	1.1276 (8)	0.1046 (6)	0.0412 (5)	0.026 (2)
H36	1.1193	0.0837	−0.0148	0.031*
C37	1.1404 (8)	0.1997 (6)	0.0873 (5)	0.024 (2)
H37	1.1396	0.2457	0.0633	0.029*
C38	1.1546 (8)	0.2298 (6)	0.1681 (5)	0.025 (2)
H38	1.1648	0.2961	0.2003	0.029*
C39	1.1537 (7)	0.1612 (6)	0.2020 (5)	0.0167 (19)
C40	1.1735 (7)	0.1829 (6)	0.2884 (5)	0.017 (2)
H40A	1.2602	0.1862	0.3039	0.021*
H40B	1.1414	0.2461	0.3181	0.021*
N9	0.7818 (6)	0.0607 (5)	0.3187 (4)	0.0193 (17)
C41	0.9123 (8)	0.0428 (6)	0.3136 (5)	0.024 (2)
H41A	0.9230	−0.0129	0.2644	0.028*
H41B	0.9426	0.0261	0.3587	0.028*
C42	0.9868 (7)	0.1289 (5)	0.3140 (5)	0.0170 (19)
H42A	0.9572	0.1457	0.2687	0.020*
H42B	0.9766	0.1848	0.3632	0.020*
N10	1.1149 (6)	0.1089 (5)	0.3091 (4)	0.0173 (16)
C43	1.1735 (8)	0.0994 (6)	0.3815 (5)	0.027 (2)
H43A	1.1176	0.1179	0.4235	0.032*
H43B	1.2446	0.1437	0.4010	0.032*
C44	1.2112 (8)	−0.0036 (7)	0.3646 (6)	0.032 (3)

O3	1.1880 (5)	−0.0656 (4)	0.2950 (4)	0.0292 (16)	
O4	1.2605 (7)	−0.0207 (5)	0.4205 (5)	0.062 (2)	
O5	−0.1995 (5)	0.6110 (4)	0.3193 (3)	0.0311 (16)	
O6	0.2956 (6)	0.3206 (4)	0.5363 (3)	0.0319 (16)	
O7	0.0772 (5)	0.3326 (4)	0.4671 (3)	0.0292 (16)	
O8	0.3234 (6)	0.1477 (5)	0.5765 (4)	0.0442 (19)	
O9	0.4745 (6)	0.2287 (4)	0.4432 (4)	0.0351 (17)	
O10	0.5598 (6)	0.1138 (5)	0.5236 (4)	0.0429 (19)	
O11	0.4555 (9)	0.1661 (7)	0.0956 (5)	0.094 (3)	
O12	0.1109 (12)	0.0290 (8)	0.5442 (7)	0.038 (3)	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0169 (6)	0.0168 (5)	0.0175 (6)	−0.0018 (4)	0.0010 (5)	0.0058 (5)
Cu2	0.0179 (6)	0.0187 (5)	0.0179 (6)	0.0006 (5)	0.0014 (5)	0.0085 (5)
Br1	0.0149 (5)	0.0429 (6)	0.0292 (6)	0.0012 (4)	0.0023 (4)	0.0136 (5)
Br2	0.0259 (6)	0.0201 (5)	0.0273 (5)	−0.0046 (4)	−0.0076 (4)	0.0071 (4)
Br3	0.0416 (7)	0.0325 (6)	0.0337 (6)	0.0059 (5)	−0.0020 (5)	0.0212 (5)
N1	0.014 (4)	0.013 (4)	0.023 (4)	−0.002 (3)	−0.005 (3)	0.006 (3)
C1	0.012 (5)	0.038 (6)	0.036 (6)	−0.002 (4)	−0.004 (4)	0.022 (5)
C2	0.028 (6)	0.024 (5)	0.028 (6)	0.001 (4)	−0.006 (5)	0.014 (5)
C3	0.015 (6)	0.044 (6)	0.056 (7)	−0.013 (5)	−0.012 (5)	0.038 (6)
C4	0.017 (5)	0.031 (5)	0.013 (5)	0.000 (4)	−0.002 (4)	0.006 (4)
C5	0.012 (5)	0.020 (5)	0.015 (5)	0.006 (4)	0.002 (4)	0.004 (4)
C6	0.009 (5)	0.025 (5)	0.014 (5)	−0.004 (4)	0.002 (4)	0.000 (4)
N2	0.012 (4)	0.012 (4)	0.037 (5)	0.000 (3)	0.004 (3)	0.007 (4)
C7	0.025 (6)	0.025 (5)	0.018 (5)	−0.006 (4)	−0.003 (4)	0.007 (4)
C8	0.019 (6)	0.044 (6)	0.022 (5)	−0.007 (5)	0.002 (4)	0.023 (5)
C9	0.018 (6)	0.031 (5)	0.036 (6)	0.001 (4)	0.001 (4)	0.026 (5)
C10	0.015 (5)	0.025 (5)	0.031 (6)	−0.003 (4)	0.011 (4)	0.013 (4)
C11	0.007 (5)	0.027 (5)	0.025 (5)	0.000 (4)	0.005 (4)	0.018 (4)
C12	0.011 (5)	0.018 (4)	0.023 (5)	0.000 (4)	0.007 (4)	0.004 (4)
N3	0.013 (4)	0.014 (4)	0.016 (4)	0.000 (3)	0.004 (3)	0.007 (3)
C13	0.011 (5)	0.022 (5)	0.033 (6)	0.005 (4)	0.008 (4)	0.015 (5)
C14	0.010 (5)	0.016 (5)	0.035 (6)	−0.002 (4)	0.009 (4)	0.000 (4)
C15	0.013 (5)	0.029 (5)	0.033 (6)	0.003 (4)	0.007 (4)	0.009 (5)
C16	0.011 (5)	0.033 (5)	0.013 (5)	0.008 (4)	0.004 (4)	0.007 (4)
C17	0.011 (5)	0.011 (4)	0.017 (5)	0.002 (3)	0.010 (4)	0.000 (4)
C18	0.008 (5)	0.029 (5)	0.019 (5)	0.006 (4)	0.002 (4)	0.015 (4)
N4	0.013 (4)	0.012 (3)	0.018 (4)	−0.002 (3)	0.003 (3)	0.001 (3)
C19	0.014 (5)	0.025 (5)	0.018 (5)	0.006 (4)	0.004 (4)	0.005 (4)
C20	0.011 (5)	0.021 (4)	0.020 (5)	−0.002 (4)	0.000 (4)	0.013 (4)
N5	0.009 (4)	0.017 (4)	0.017 (4)	0.002 (3)	−0.002 (3)	0.003 (3)
C21	0.016 (5)	0.016 (5)	0.024 (5)	−0.001 (4)	0.000 (4)	0.002 (4)
C22	0.004 (5)	0.037 (6)	0.021 (5)	0.003 (4)	−0.002 (4)	0.005 (5)
O1	0.016 (4)	0.027 (3)	0.016 (3)	−0.004 (3)	−0.002 (3)	0.009 (3)
O2	0.052 (5)	0.034 (4)	0.027 (4)	0.003 (3)	0.010 (4)	0.002 (3)

Cu3	0.0218 (7)	0.0166 (5)	0.0248 (6)	0.0003 (5)	0.0058 (5)	0.0066 (5)
Cu4	0.0207 (7)	0.0143 (5)	0.0272 (6)	0.0030 (5)	0.0062 (5)	0.0087 (5)
Br4	0.0209 (6)	0.0246 (5)	0.0360 (6)	0.0025 (4)	0.0038 (4)	0.0076 (4)
Br5	0.0682 (9)	0.0290 (5)	0.0333 (6)	−0.0026 (5)	0.0200 (6)	0.0132 (5)
Br6	0.0423 (7)	0.0168 (5)	0.0332 (6)	−0.0038 (4)	0.0032 (5)	0.0081 (4)
N6	0.018 (4)	0.018 (4)	0.030 (5)	0.001 (3)	0.006 (3)	0.007 (4)
C23	0.030 (6)	0.029 (5)	0.027 (6)	−0.011 (4)	0.006 (5)	0.011 (5)
C24	0.014 (5)	0.028 (5)	0.031 (6)	0.001 (4)	0.007 (4)	0.002 (5)
C25	0.030 (6)	0.017 (5)	0.058 (8)	0.000 (4)	0.013 (5)	0.016 (5)
C26	0.017 (6)	0.022 (5)	0.050 (7)	0.003 (4)	0.007 (5)	0.022 (5)
C27	0.006 (5)	0.028 (5)	0.029 (6)	−0.001 (4)	0.006 (4)	0.012 (5)
C28	0.012 (5)	0.027 (5)	0.034 (6)	0.000 (4)	0.008 (4)	0.015 (4)
N7	0.022 (5)	0.017 (4)	0.027 (5)	0.006 (3)	0.006 (4)	0.006 (3)
C29	0.017 (5)	0.031 (5)	0.038 (6)	−0.005 (4)	0.002 (4)	0.021 (5)
C30	0.033 (7)	0.014 (5)	0.047 (7)	−0.003 (4)	0.003 (5)	0.006 (5)
C31	0.027 (6)	0.022 (5)	0.043 (7)	−0.003 (4)	0.009 (5)	−0.005 (5)
C32	0.013 (5)	0.034 (6)	0.031 (6)	−0.002 (4)	0.003 (4)	0.004 (5)
C33	0.014 (5)	0.023 (5)	0.028 (6)	−0.002 (4)	0.010 (4)	0.005 (4)
C34	0.021 (6)	0.031 (5)	0.026 (5)	0.003 (4)	0.012 (4)	0.014 (4)
N8	0.012 (4)	0.016 (4)	0.022 (4)	−0.003 (3)	0.003 (3)	0.003 (3)
C35	0.015 (5)	0.033 (5)	0.023 (6)	−0.006 (4)	−0.001 (4)	0.008 (5)
C36	0.027 (6)	0.033 (6)	0.027 (5)	0.005 (4)	0.008 (4)	0.020 (5)
C37	0.029 (6)	0.019 (5)	0.033 (6)	0.008 (4)	0.007 (5)	0.017 (4)
C38	0.025 (6)	0.023 (5)	0.026 (6)	−0.003 (4)	0.008 (4)	0.009 (4)
C39	0.009 (5)	0.016 (4)	0.022 (5)	−0.002 (4)	0.008 (4)	0.002 (4)
C40	0.016 (5)	0.017 (4)	0.022 (5)	−0.003 (4)	0.005 (4)	0.011 (4)
N9	0.009 (4)	0.026 (4)	0.026 (4)	0.000 (3)	0.002 (3)	0.012 (4)
C41	0.019 (6)	0.025 (5)	0.023 (5)	−0.002 (4)	0.003 (4)	0.004 (4)
C42	0.012 (5)	0.014 (4)	0.023 (5)	−0.006 (4)	0.007 (4)	0.004 (4)
N10	0.003 (4)	0.022 (4)	0.027 (4)	−0.001 (3)	0.001 (3)	0.010 (3)
C43	0.028 (6)	0.024 (5)	0.033 (6)	−0.006 (4)	−0.004 (5)	0.018 (5)
C44	0.016 (6)	0.046 (7)	0.049 (7)	−0.009 (5)	−0.008 (5)	0.036 (6)
O3	0.021 (4)	0.025 (3)	0.047 (5)	−0.001 (3)	0.002 (3)	0.020 (3)
O4	0.077 (6)	0.050 (5)	0.064 (6)	−0.005 (4)	−0.034 (5)	0.036 (4)
O5	0.016 (4)	0.043 (4)	0.027 (4)	−0.001 (3)	0.003 (3)	0.006 (3)
O6	0.027 (4)	0.042 (4)	0.023 (4)	−0.001 (3)	0.003 (3)	0.009 (3)
O7	0.025 (4)	0.030 (4)	0.030 (4)	0.000 (3)	0.003 (3)	0.008 (3)
O8	0.056 (5)	0.047 (4)	0.037 (4)	−0.009 (4)	−0.001 (4)	0.024 (4)
O9	0.027 (4)	0.042 (4)	0.036 (4)	0.010 (3)	0.011 (3)	0.014 (3)
O10	0.051 (5)	0.042 (4)	0.043 (4)	0.007 (4)	0.006 (4)	0.025 (4)
O11	0.101 (9)	0.129 (9)	0.076 (7)	0.025 (7)	0.002 (6)	0.065 (7)
O12	0.056 (10)	0.022 (7)	0.037 (8)	0.000 (6)	−0.002 (7)	0.015 (6)

Geometric parameters (Å, º)

Cu1—N1	1.982 (7)	Cu3—N6	1.998 (7)
Cu1—N2	1.989 (7)	Cu3—N7	1.986 (7)
Cu1—N4	2.133 (6)	Cu3—N9	2.075 (7)

Cu2—O1	1.944 (5)	Cu3—Br4	2.7342 (15)
Cu1—Br2	2.4361 (13)	Cu3—Br5	2.4102 (14)
Cu1—Br1	2.5228 (14)	Cu4—N8	1.955 (7)
Cu2—N3	1.970 (6)	Cu4—N10	2.023 (7)
Cu2—N5	2.046 (6)	Cu4—O3	1.900 (6)
Cu2—O5	2.309 (6)	Cu4—Br6	2.3496 (14)
Cu2—Br3	2.3832 (13)	N6—C23	1.337 (11)
N1—C5	1.340 (10)	N6—C27	1.343 (11)
N1—C1	1.343 (10)	C23—C24	1.378 (12)
C1—C2	1.371 (11)	C23—H23	0.9500
C1—H1	0.9500	C24—C25	1.375 (12)
C2—C3	1.371 (13)	C24—H24	0.9500
C2—H2	0.9500	C25—C26	1.387 (13)
C3—C4	1.391 (12)	C25—H25	0.9500
C3—H3	0.9500	C26—C27	1.365 (11)
C4—C5	1.395 (11)	C26—H26	0.9500
C4—H4	0.9500	C27—C28	1.509 (12)
C5—C6	1.515 (11)	C28—N9	1.494 (10)
C6—N4	1.475 (10)	C28—H28A	0.9900
C6—H6A	0.9900	C28—H28B	0.9900
C6—H6B	0.9900	N7—C33	1.340 (11)
N2—C11	1.326 (10)	N7—C29	1.365 (10)
N2—C7	1.359 (11)	C29—C30	1.367 (12)
C7—C8	1.389 (11)	C29—H29	0.9500
C7—H7	0.9500	C30—C31	1.386 (13)
C8—C9	1.347 (12)	C30—H30	0.9500
C8—H8	0.9500	C31—C32	1.381 (12)
C9—C10	1.369 (12)	C31—H31	0.9500
C9—H9	0.9500	C32—C33	1.390 (12)
C10—C11	1.405 (11)	C32—H32	0.9500
C10—H10	0.9500	C33—C34	1.527 (11)
C11—C12	1.504 (11)	C34—N9	1.500 (10)
C12—N4	1.487 (10)	C34—H34A	0.9900
C12—H12A	0.9900	C34—H34B	0.9900
C12—H12B	0.9900	N8—C35	1.336 (10)
N3—C13	1.325 (10)	N8—C39	1.375 (10)
N3—C17	1.343 (9)	C35—C36	1.385 (11)
C13—C14	1.383 (12)	C35—H35	0.9500
C13—H13	0.9500	C36—C37	1.362 (11)
C14—C15	1.364 (12)	C36—H36	0.9500
C14—H14	0.9500	C37—C38	1.371 (12)
C15—C16	1.409 (11)	C37—H37	0.9500
C15—H15	0.9500	C38—C39	1.392 (11)
C16—C17	1.388 (11)	C38—H38	0.9500
C16—H16	0.9500	C39—C40	1.489 (11)
C17—C18	1.500 (10)	C40—N10	1.471 (10)
C18—N5	1.474 (10)	C40—H40A	0.9900
C18—H18A	0.9900	C40—H40B	0.9900

C18—H18B	0.9900	N9—C41	1.498 (10)
N4—C19	1.485 (10)	C41—C42	1.535 (11)
C19—C20	1.532 (11)	C41—H41A	0.9900
C19—H19A	0.9900	C41—H41B	0.9900
C19—H19B	0.9900	C42—N10	1.477 (10)
C20—N5	1.513 (10)	C42—H42A	0.9900
C20—H20A	0.9900	C42—H42B	0.9900
C20—H20B	0.9900	N10—C43	1.492 (10)
N5—C21	1.488 (9)	C43—C44	1.534 (12)
C21—C22	1.501 (11)	C43—H43A	0.9900
C21—H21A	0.9900	C43—H43B	0.9900
C21—H21B	0.9900	C44—O4	1.240 (11)
C22—O2	1.248 (10)	C44—O3	1.271 (11)
C22—O1	1.292 (10)		

N1—Cu1—N2	163.4 (3)	O1—C22—C21	118.1 (7)
N1—Cu1—N4	81.7 (3)	C22—O1—Cu2	113.7 (5)
N2—Cu1—N4	82.1 (3)	N7—Cu3—N6	164.5 (3)
N1—Cu1—Br2	95.53 (19)	N7—Cu3—N9	82.7 (3)
N2—Cu1—Br2	97.3 (2)	N6—Cu3—N9	82.1 (3)
N4—Cu1—Br2	127.66 (18)	N7—Cu3—Br5	96.3 (2)
N1—Cu1—Br1	90.5 (2)	N6—Cu3—Br5	97.4 (2)
N2—Cu1—Br1	92.5 (2)	N9—Cu3—Br5	141.93 (19)
N4—Cu1—Br1	113.38 (18)	N7—Cu3—Br4	91.0 (2)
Br2—Cu1—Br1	118.91 (5)	N6—Cu3—Br4	88.7 (2)
O1—Cu2—N3	166.6 (2)	N9—Cu3—Br4	99.52 (19)
O1—Cu2—N5	83.8 (2)	Br5—Cu3—Br4	118.54 (5)
N3—Cu2—N5	84.0 (3)	O3—Cu4—N8	156.6 (3)
O1—Cu2—O5	86.6 (2)	O3—Cu4—N10	86.3 (3)
N3—Cu2—O5	88.4 (2)	N8—Cu4—N10	84.2 (3)
N5—Cu2—O5	92.0 (2)	O3—Cu4—Br6	98.34 (19)
O1—Cu2—Br3	93.36 (17)	N8—Cu4—Br6	100.6 (2)
N3—Cu2—Br3	99.98 (19)	N10—Cu4—Br6	149.85 (19)
N5—Cu2—Br3	148.96 (19)	C23—N6—C27	119.2 (7)
O5—Cu2—Br3	118.76 (16)	C23—N6—Cu3	127.5 (6)
C5—N1—C1	119.1 (7)	C27—N6—Cu3	113.3 (6)
C5—N1—Cu1	113.8 (5)	N6—C23—C24	121.8 (9)
C1—N1—Cu1	127.1 (6)	N6—C23—H23	119.1
N1—C1—C2	121.3 (8)	C24—C23—H23	119.1
N1—C1—H1	119.3	C25—C24—C23	119.4 (9)
C2—C1—H1	119.3	C25—C24—H24	120.3
C3—C2—C1	120.4 (8)	C23—C24—H24	120.3
C3—C2—H2	119.8	C24—C25—C26	118.2 (8)
C1—C2—H2	119.8	C24—C25—H25	120.9
C2—C3—C4	119.0 (8)	C26—C25—H25	120.9
C2—C3—H3	120.5	C27—C26—C25	120.0 (9)
C4—C3—H3	120.5	C27—C26—H26	120.0
C3—C4—C5	117.9 (8)	C25—C26—H26	120.0

C3—C4—H4	121.0	N6—C27—C26	121.4 (8)
C5—C4—H4	121.0	N6—C27—C28	115.7 (8)
N1—C5—C4	122.3 (7)	C26—C27—C28	122.9 (8)
N1—C5—C6	115.1 (7)	N9—C28—C27	108.8 (7)
C4—C5—C6	122.6 (7)	N9—C28—H28A	109.9
N4—C6—C5	108.8 (6)	C27—C28—H28A	109.9
N4—C6—H6A	109.9	N9—C28—H28B	109.9
C5—C6—H6A	109.9	C27—C28—H28B	109.9
N4—C6—H6B	109.9	H28A—C28—H28B	108.3
C5—C6—H6B	109.9	C33—N7—C29	117.5 (8)
H6A—C6—H6B	108.3	C33—N7—Cu3	115.4 (5)
C11—N2—C7	120.3 (7)	C29—N7—Cu3	127.1 (6)
C11—N2—Cu1	114.8 (6)	N7—C29—C30	122.0 (9)
C7—N2—Cu1	124.9 (6)	N7—C29—H29	119.0
N2—C7—C8	120.6 (8)	C30—C29—H29	119.0
N2—C7—H7	119.7	C29—C30—C31	119.9 (9)
C8—C7—H7	119.7	C29—C30—H30	120.1
C9—C8—C7	119.4 (9)	C31—C30—H30	120.1
C9—C8—H8	120.3	C32—C31—C30	119.0 (9)
C7—C8—H8	120.3	C32—C31—H31	120.5
C8—C9—C10	120.1 (8)	C30—C31—H31	120.5
C8—C9—H9	120.0	C31—C32—C33	118.2 (9)
C10—C9—H9	120.0	C31—C32—H32	120.9
C9—C10—C11	119.5 (8)	C33—C32—H32	120.9
C9—C10—H10	120.2	N7—C33—C32	123.4 (8)
C11—C10—H10	120.2	N7—C33—C34	116.2 (7)
N2—C11—C10	120.0 (8)	C32—C33—C34	120.4 (8)
N2—C11—C12	118.3 (7)	N9—C34—C33	110.1 (7)
C10—C11—C12	121.6 (8)	N9—C34—H34A	109.6
N4—C12—C11	110.0 (6)	C33—C34—H34A	109.6
N4—C12—H12A	109.7	N9—C34—H34B	109.6
C11—C12—H12A	109.7	C33—C34—H34B	109.6
N4—C12—H12B	109.7	H34A—C34—H34B	108.2
C11—C12—H12B	109.7	C35—N8—C39	118.5 (7)
H12A—C12—H12B	108.2	C35—N8—Cu4	128.3 (6)
C13—N3—C17	118.3 (7)	C39—N8—Cu4	113.2 (6)
C13—N3—Cu2	128.9 (6)	N8—C35—C36	122.4 (8)
C17—N3—Cu2	112.8 (5)	N8—C35—H35	118.8
N3—C13—C14	123.6 (8)	C36—C35—H35	118.8
N3—C13—H13	118.2	C37—C36—C35	118.8 (9)
C14—C13—H13	118.2	C37—C36—H36	120.6
C15—C14—C13	118.1 (8)	C35—C36—H36	120.6
C15—C14—H14	121.0	C36—C37—C38	120.7 (8)
C13—C14—H14	121.0	C36—C37—H37	119.7
C14—C15—C16	120.1 (8)	C38—C37—H37	119.7
C14—C15—H15	120.0	C37—C38—C39	118.6 (8)
C16—C15—H15	120.0	C37—C38—H38	120.7
C17—C16—C15	117.2 (8)	C39—C38—H38	120.7

C17—C16—H16	121.4	N8—C39—C38	121.0 (8)
C15—C16—H16	121.4	N8—C39—C40	114.4 (7)
N3—C17—C16	122.7 (7)	C38—C39—C40	124.5 (7)
N3—C17—C18	116.0 (7)	N10—C40—C39	110.9 (7)
C16—C17—C18	121.3 (7)	N10—C40—H40A	109.5
N5—C18—C17	110.3 (6)	C39—C40—H40A	109.5
N5—C18—H18A	109.6	N10—C40—H40B	109.5
C17—C18—H18A	109.6	C39—C40—H40B	109.5
N5—C18—H18B	109.6	H40A—C40—H40B	108.0
C17—C18—H18B	109.6	C28—N9—C41	108.8 (6)
H18A—C18—H18B	108.1	C28—N9—C34	112.6 (6)
C6—N4—C19	107.8 (6)	C41—N9—C34	112.1 (6)
C6—N4—C12	112.9 (6)	C28—N9—Cu3	103.6 (5)
C19—N4—C12	113.4 (6)	C41—N9—Cu3	112.4 (5)
C6—N4—Cu1	101.2 (4)	C34—N9—Cu3	107.1 (5)
C19—N4—Cu1	115.2 (5)	N9—C41—C42	113.5 (7)
C12—N4—Cu1	105.9 (5)	N9—C41—H41A	108.9
N4—C19—C20	111.8 (7)	C42—C41—H41A	108.9
N4—C19—H19A	109.3	N9—C41—H41B	108.9
C20—C19—H19A	109.3	C42—C41—H41B	108.9
N4—C19—H19B	109.3	H41A—C41—H41B	107.7
C20—C19—H19B	109.3	N10—C42—C41	112.1 (6)
H19A—C19—H19B	107.9	N10—C42—H42A	109.2
N5—C20—C19	110.1 (6)	C41—C42—H42A	109.2
N5—C20—H20A	109.6	N10—C42—H42B	109.2
C19—C20—H20A	109.6	C41—C42—H42B	109.2
N5—C20—H20B	109.6	H42A—C42—H42B	107.9
C19—C20—H20B	109.6	C40—N10—C42	108.2 (6)
H20A—C20—H20B	108.1	C40—N10—C43	112.9 (6)
C18—N5—C21	114.4 (6)	C42—N10—C43	113.5 (7)
C18—N5—C20	108.2 (6)	C40—N10—Cu4	105.3 (5)
C21—N5—C20	111.8 (6)	C42—N10—Cu4	109.3 (5)
C18—N5—Cu2	104.4 (5)	C43—N10—Cu4	107.2 (5)
C21—N5—Cu2	105.4 (5)	N10—C43—C44	111.2 (7)
C20—N5—Cu2	112.5 (4)	N10—C43—H43A	109.4
N5—C21—C22	110.9 (7)	C44—C43—H43A	109.4
N5—C21—H21A	109.5	N10—C43—H43B	109.4
C22—C21—H21A	109.5	C44—C43—H43B	109.4
N5—C21—H21B	109.5	H43A—C43—H43B	108.0
C22—C21—H21B	109.5	O4—C44—O3	124.6 (9)
H21A—C21—H21B	108.1	O4—C44—C43	117.4 (9)
O2—C22—O1	121.5 (8)	O3—C44—C43	118.0 (8)
O2—C22—C21	120.4 (8)	C44—O3—Cu4	115.6 (6)